Characterizing the electronic and optical properties of semiconductors

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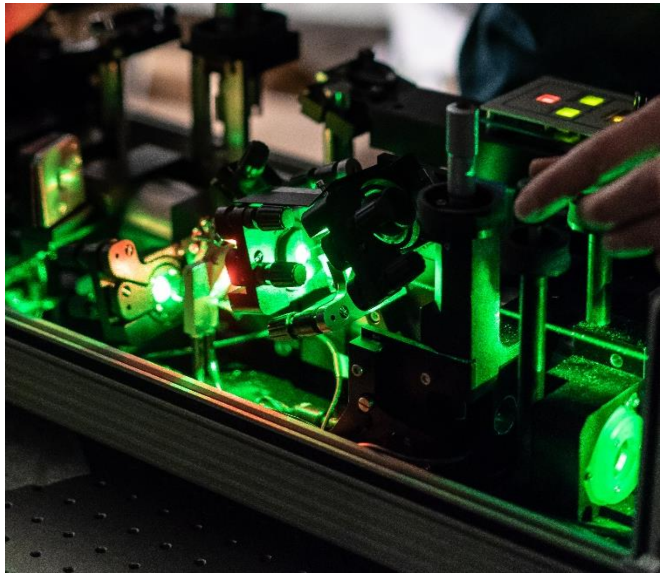
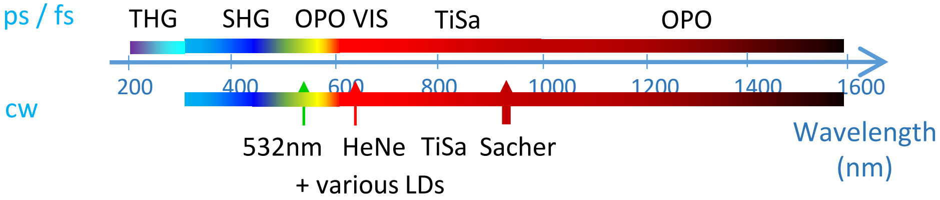
MATEPI Summer School
Porquerolles - June 2025

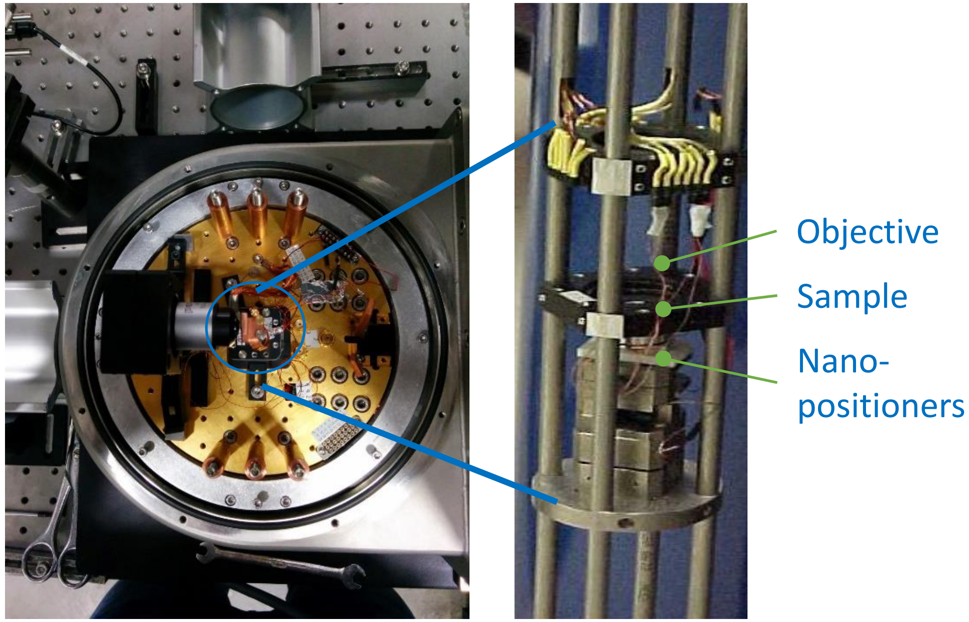
LPCNO lab – OPTO team

Laser

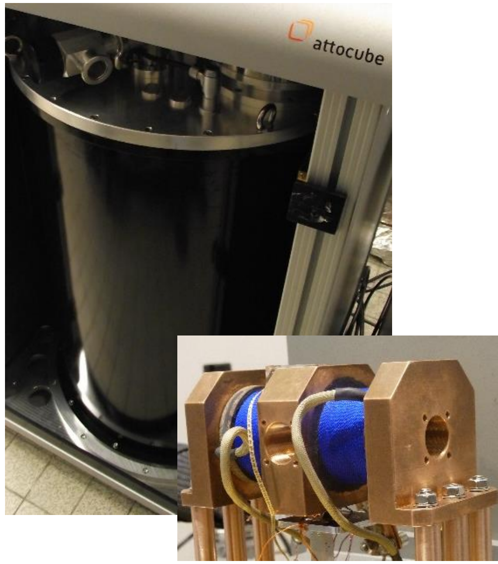




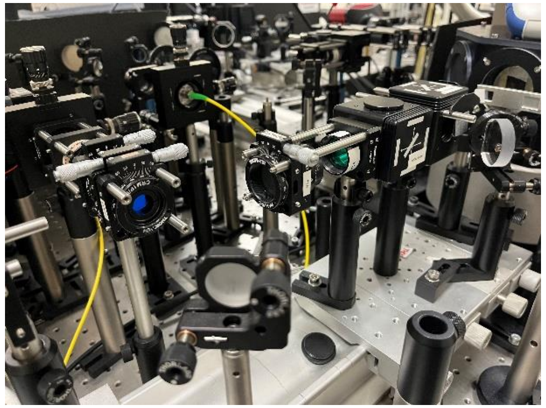
Cryostat 4K



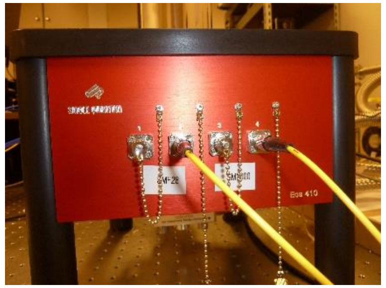
Magnetic field



Optics



Spectrometer / Detector

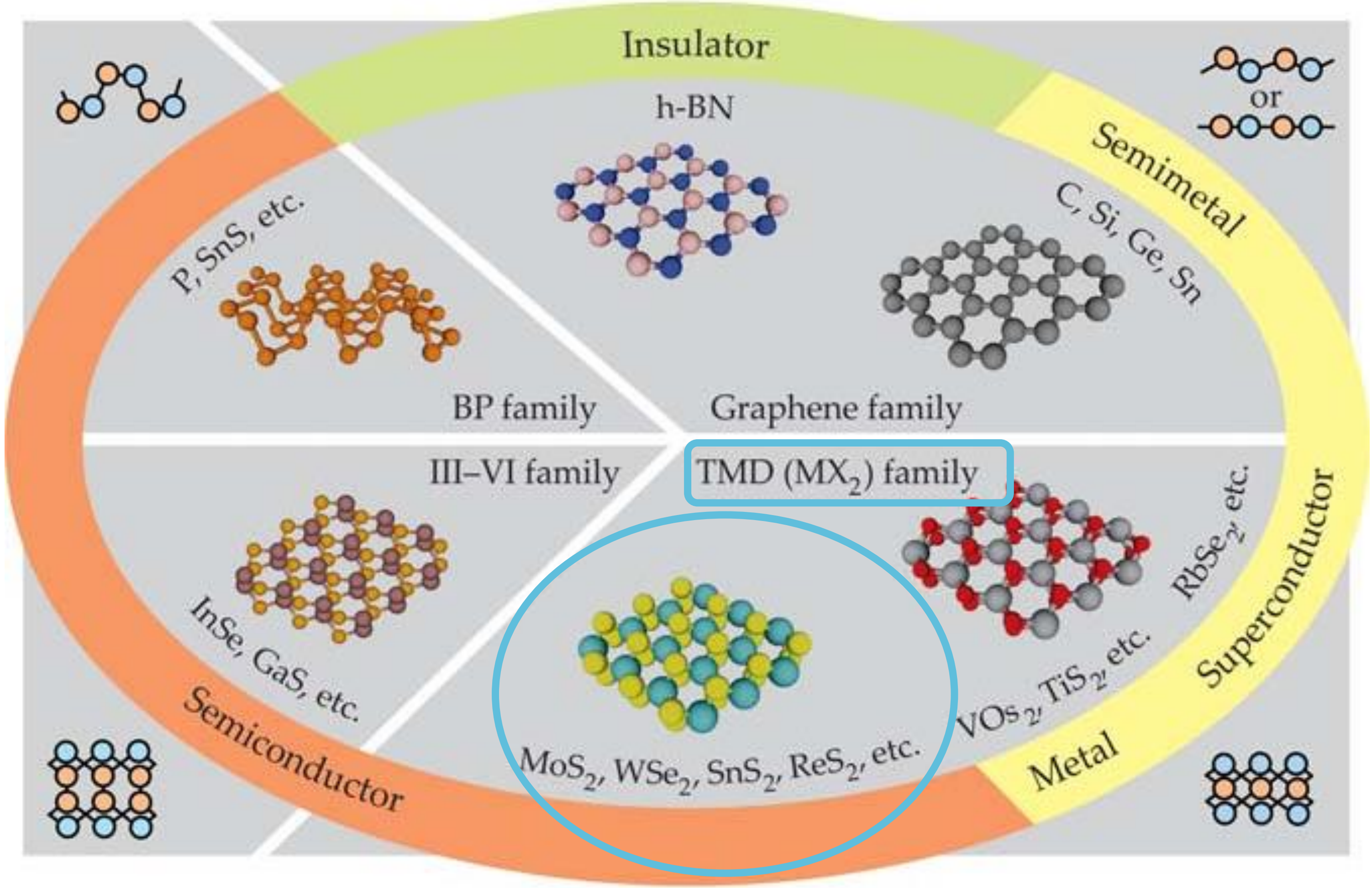


Introduction

- Large variety of methods that exploit light-matter interactions across the entire electromagnetic spectrum

- This presentation aims to give an overview of some available techniques and their potential applications for electronic and optical characterization of semiconductor epitaxial layers or micro/nanostructures

TMDC


Insulator
h-BN
Semimetal
or
C, Si, Ge, Sn
P, SnS, etc.
BP family
Graphene family
III–VI family
TMD (MX_2) family
$RbSe_2$, etc.
Superconductor
InSe, GaS, etc.
Semiconductor
MoS_2, WSe_2, SnS_2, ReS_2, etc.
VOs_2, TiS_2, etc.
Metal

Outline

Basics of SC physics

* SC band structure
Density of states
Doping

* Interaction with light

* Dimensionality

Optical characterization of SC structures

* Absorption
* Photoemission

* Reflectivity

* Photoluminescence (PL)
– PL Eexcitation (PLE)

* Time-Resolved PL
– TR-Cathodoluminescence

Electric/Optical characterization of SC structures

* Electroluminescence (EL)
* Photocurrent (PC)

Raman spectroscopy

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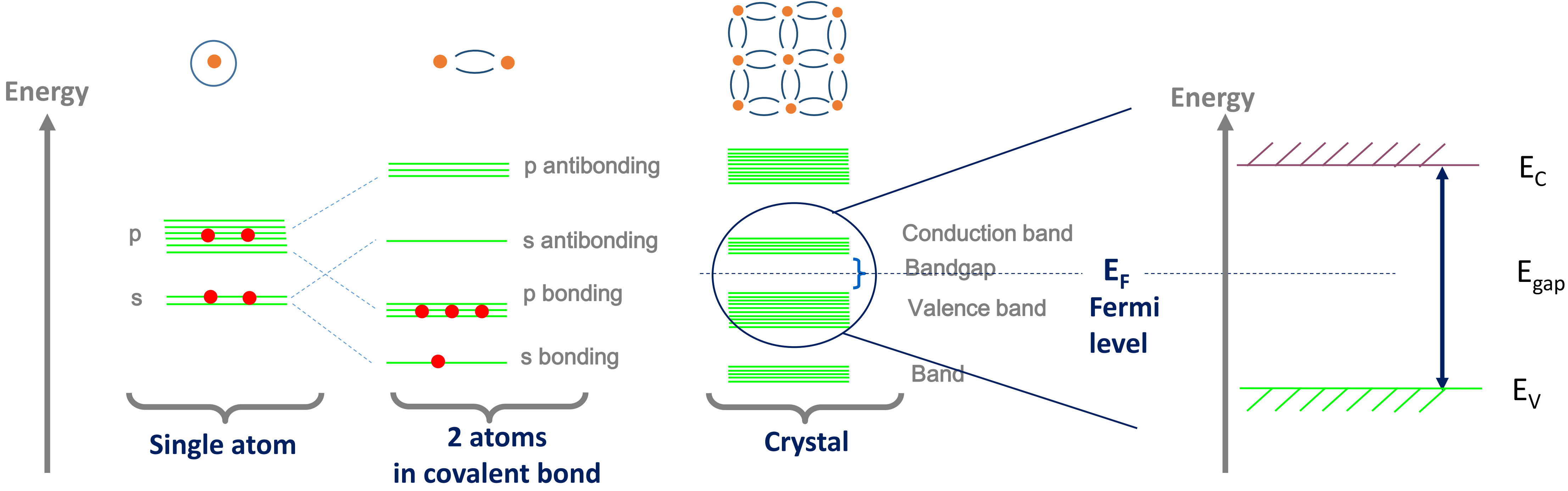
Raman spectroscopy

Band structure



Electrons in atom

- Electrons can be described by Schrödinger equation
- Ground vs excited state
- Pauli exclusion principle

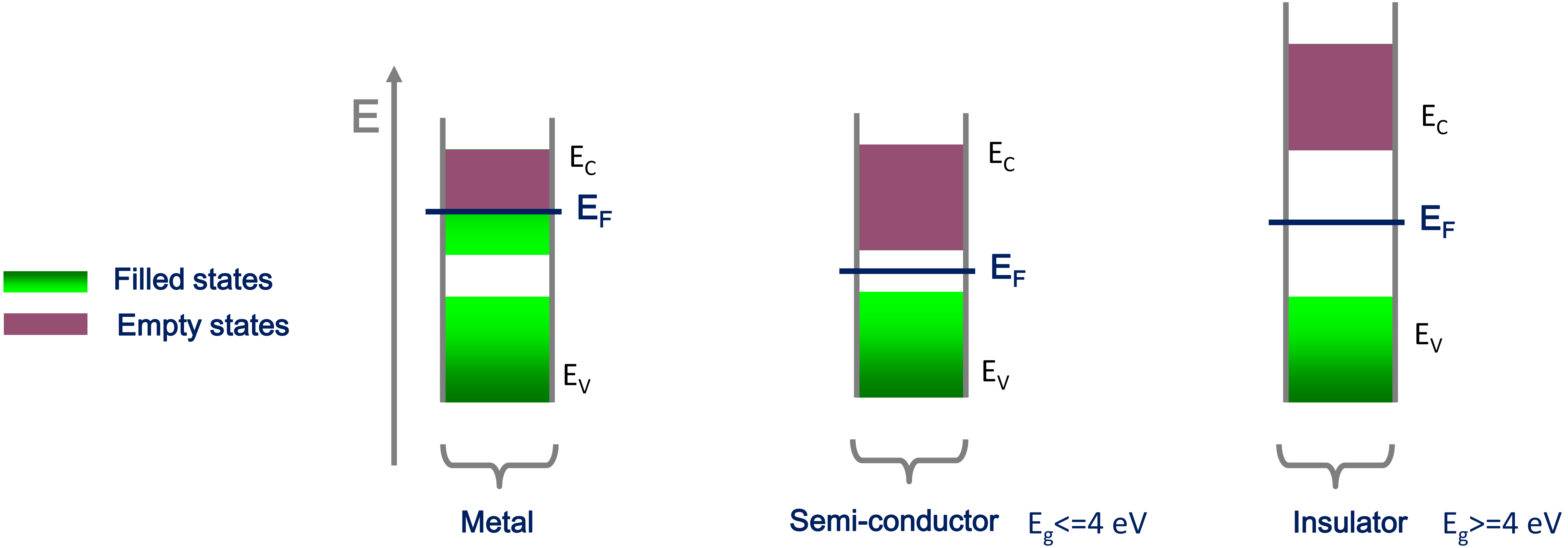
Electrons in interacting atoms

- Outer orbitals of the atoms overlap and interact strongly

Electrons in crystal

- Highest nearly-filled band : **valence band**
- Lowest nearly-empty band : **conduction band**

Band structure

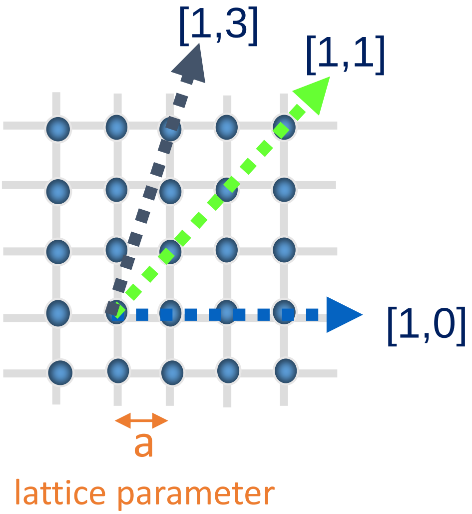


Conductivity (Ω.cm)	10^{14} - 10^{22}	10^{-6}	10^{-2} - 10^{6}

- metal: weakly bound electrons → free mobile electrons
- insulator: every electrons bound to the lattice
- semiconductor: some electrons can gain enough E to get into the conduction band

Band structure

Crystal symmetry



32 classes of crystal according to their point group symmetry
(invariance by translations, rotations…)

Crystal symmetry will affect electronic wavefunctions and optical and transport properties

Crystal periodicity

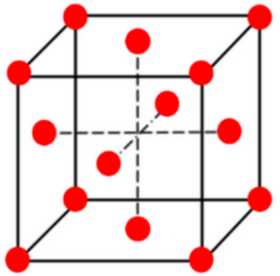
Periodic arrangement of atoms in a crystal → periodic potential $V(\vec{r}+\vec{R}) = V(\vec{r})$
with $\vec{R}$ reciprocal lattice vector

Wavefunctions of an electron in a crystal

Block's theorem $$\boxed{\psi_{n,\vec{k}}(\vec{r}) = u_{n,k} e^{i\vec{k}.\vec{r}}}$$

$\vec{k}$: wave vector in reciprocal space (linked to crystal translation invariance)
$u_{n,k}$ has the periodicity of the crystal lattice $u_{n,k}(\vec{r}+\vec{R}) = u_{n,k}(\vec{r})$

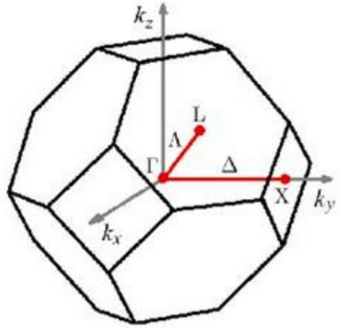
Real space



Cubic face centered

→

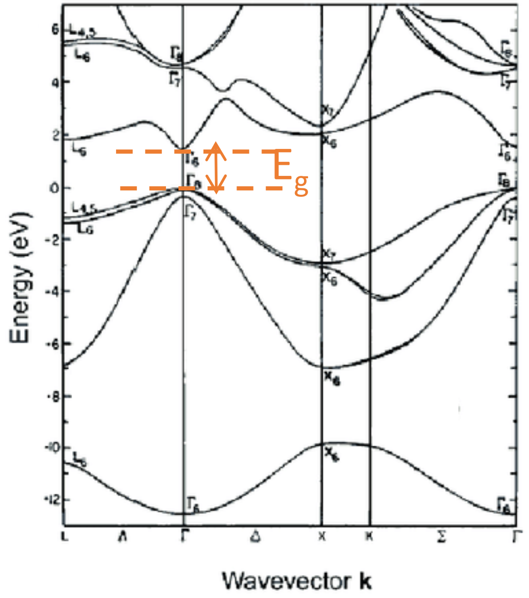
Reciprocal space



Band structure

Optical properties : consider only the band structure in a region close to band extrema, near $\vec{k}$=0, center of Brillouin zone

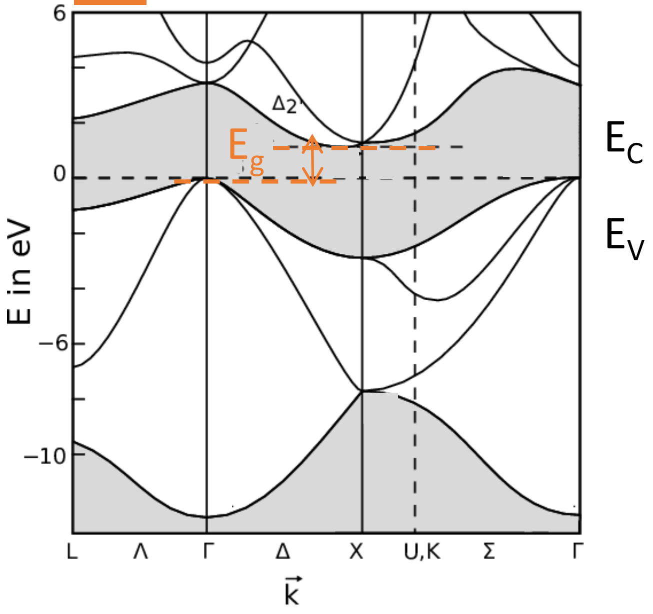
GaAs



GaAs: E_g=1.43 eV (300K)

Direct Bandgap

Si



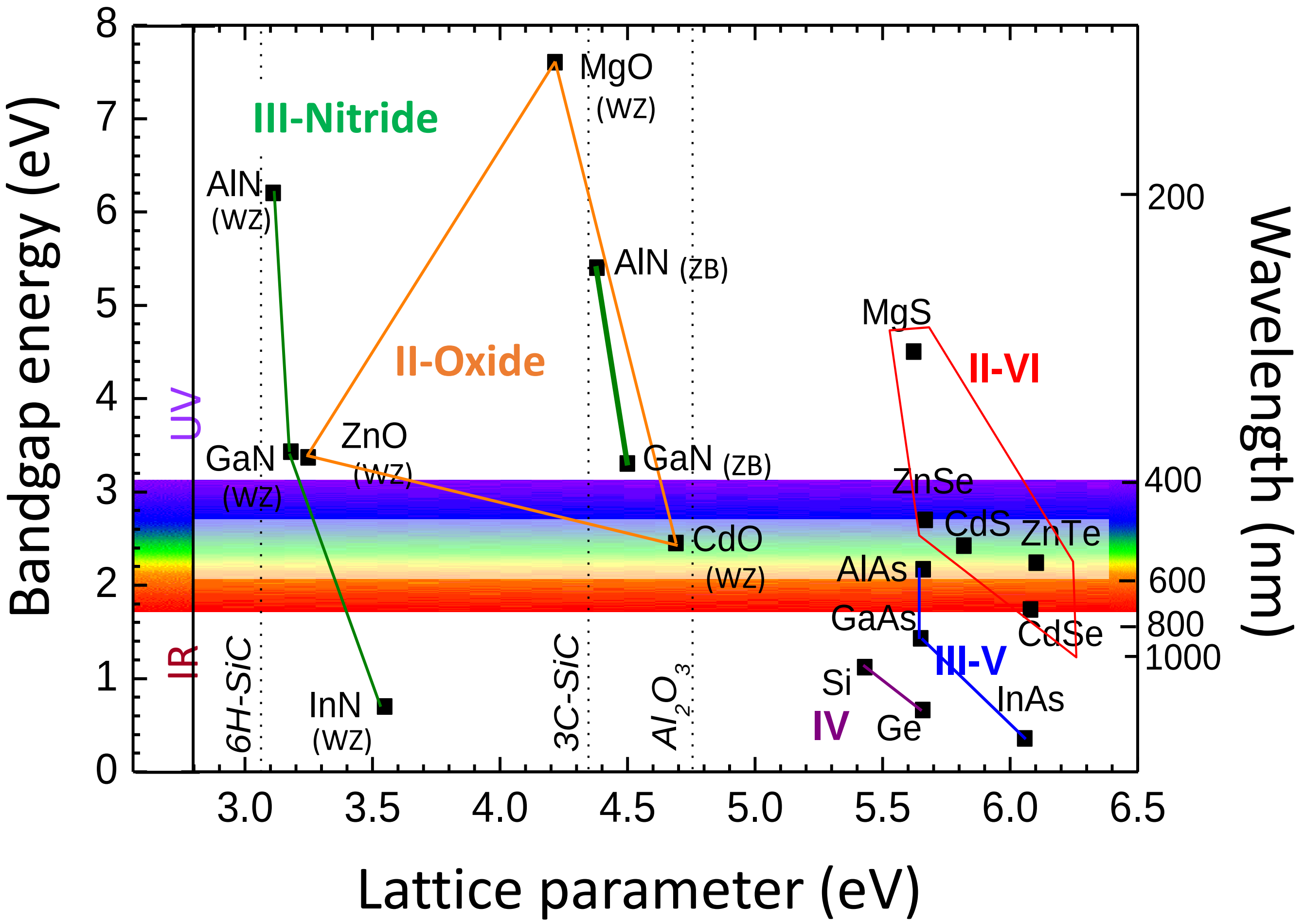
Silicon: E_g=1.1 eV

Indirect Bandgap

Max of VB and min of CB occur at the same point of the first Brillouin zone

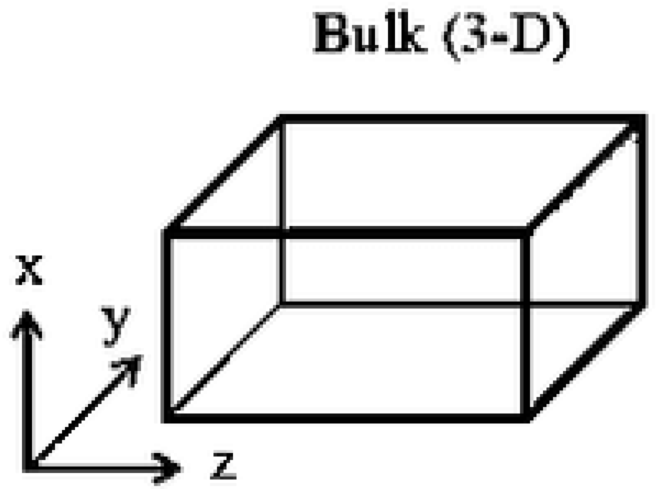
→ **Strong interaction with light**

Bandgap engineering



Density of states

for 3D crystal

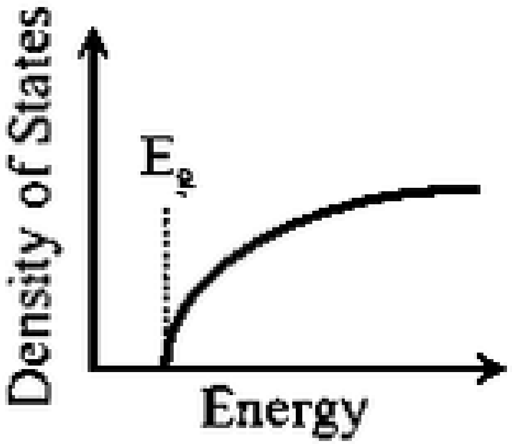


CB

$$\rho(E)_c = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E-E_c}$$

VB

$$\rho(E)_v = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E_v-E}$$



The density of states ρ(E) is a completely different function of carrier energy for 3D bulk, 2D quantum wells or 0D quantum dots

Carrier density

Carrier density linked to probability of occupation of each electronic states at thermal equilibrium

$$n_0 = \int_{E_c}^{\infty} \rho_c(E) f(E) dE$$

$$p_0 = \int_{-\infty}^{E_v} \rho_v(E)[1 - f(E)] dE$$

Concentration of electrons/holes per unit volume:

$$n_0 = N_c e^{(E_F - E_c)/kT}$$

$$p_0 = N_v e^{(E_v - E_F)/kT}$$

with

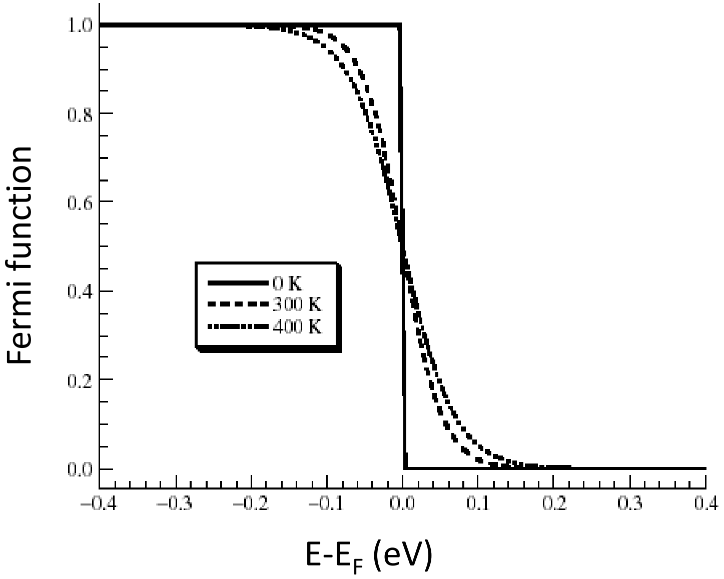
$$\begin{cases} N_c = 2\left(\dfrac{2\pi m_n^* kT}{h^2}\right)^{3/2} \\ N_v = 2\left(\dfrac{2\pi m_p^* kT}{h^2}\right)^{3/2} \\ E_F = E_C + \mathrm{kT}\ \ln\left(\dfrac{n_0}{N_c}\right) \end{cases}$$

Fermi-Dirac statistics

$$f(E) = \frac{1}{1 + e^{(E - E_F)/kT}}$$

takes into account
Pauli exclusion principle
(one fermion per state)

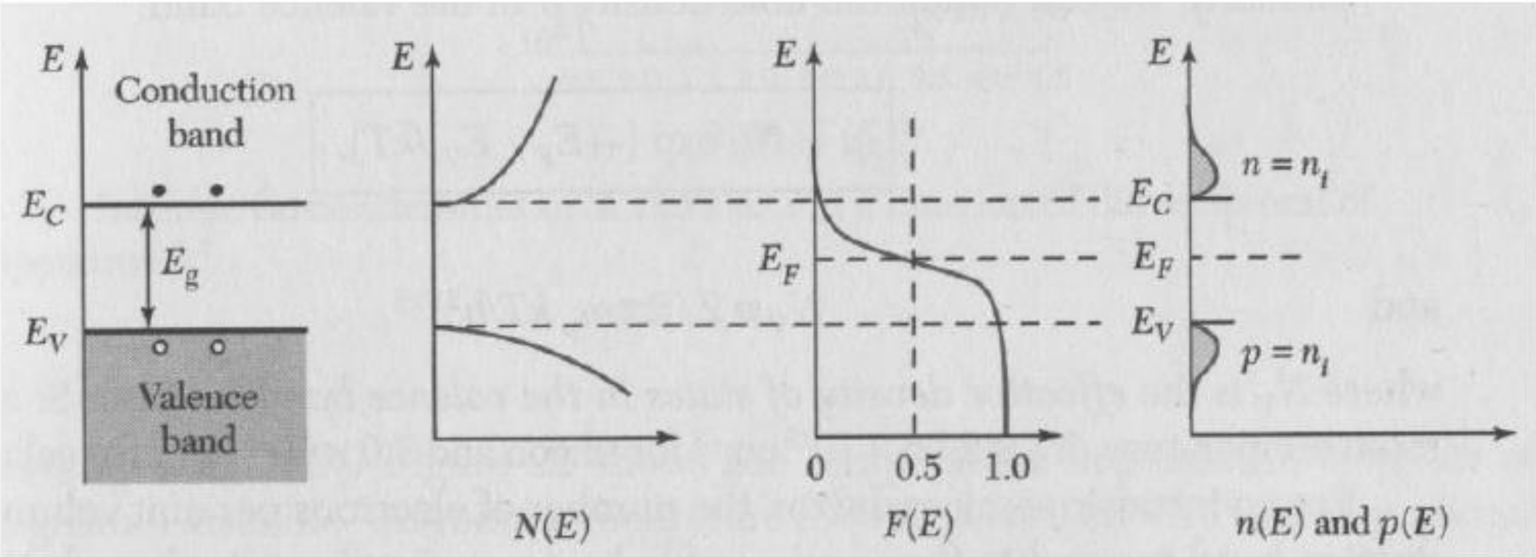
E_F : Fermi Energy



Summary

Semiconductor band diagram

Fermi distribution function



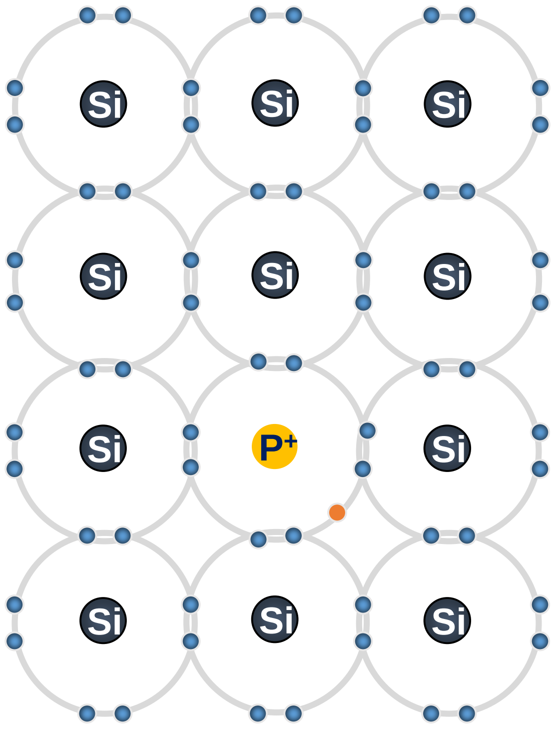
Density of states
Density of allowed states per energy range

Carrier concentration

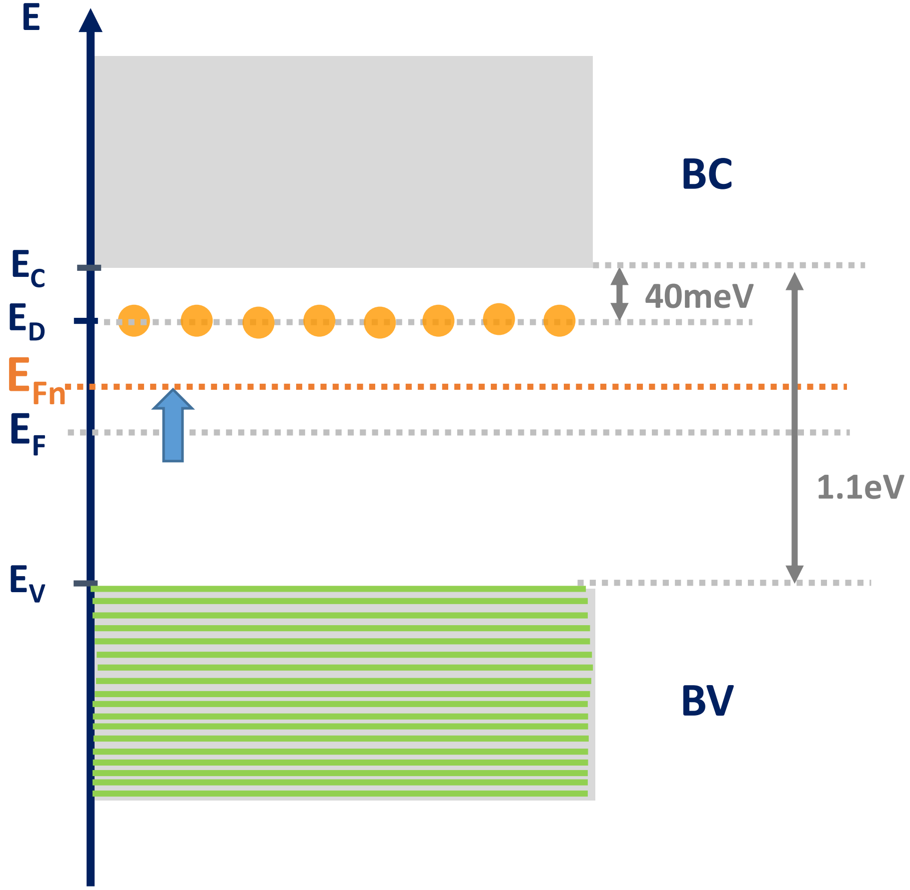
$$n = \int_{E_C}^{\infty} N(E)F(E)dE$$

Defects and Doping in SC

n-doping



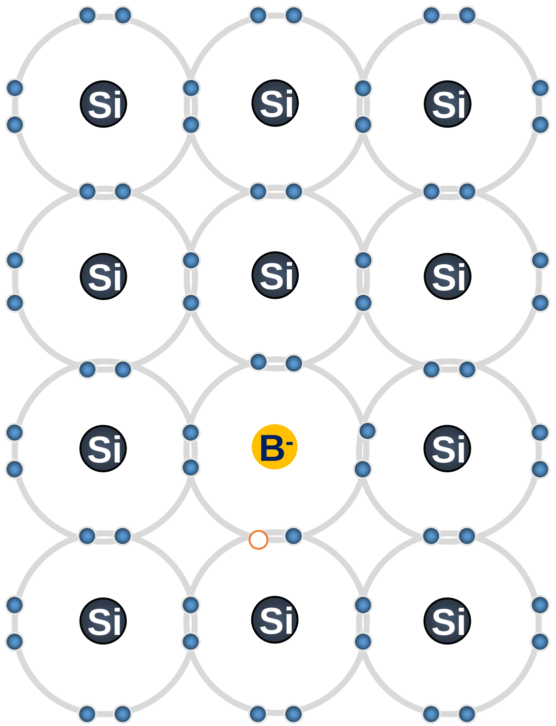
P atom → $P^+_{fixed} + e^-_{free}$



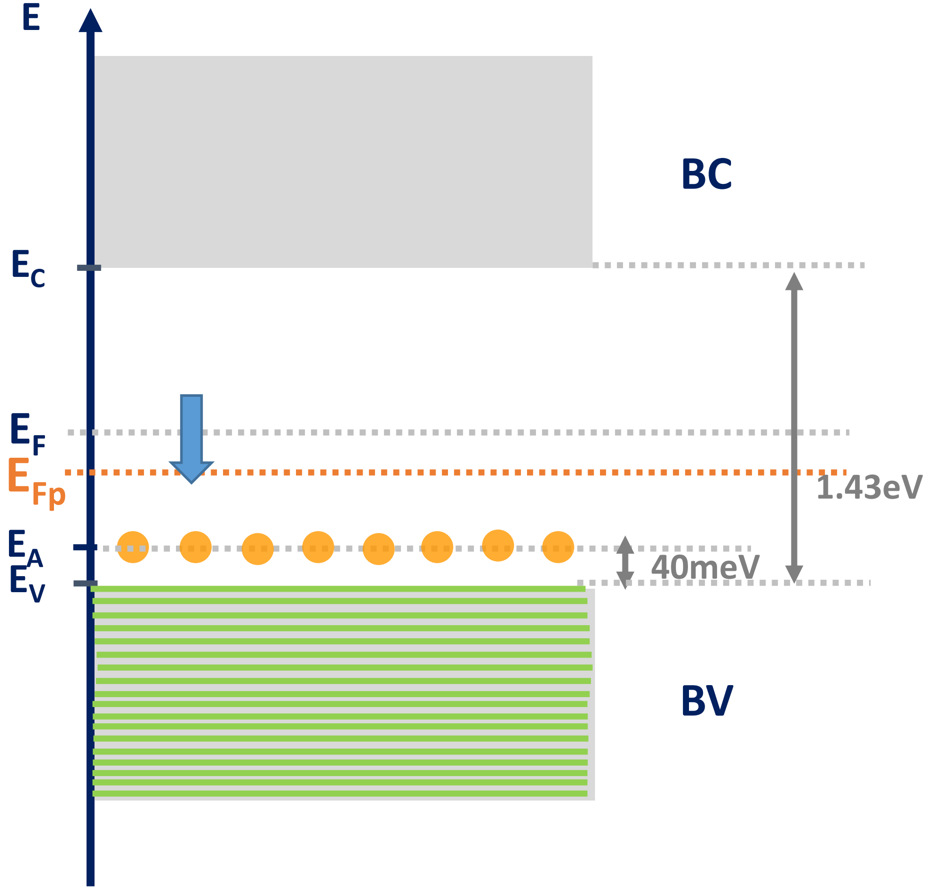
Concentration $n=N_D$ density of dopants

Defects and Doping in SC

p-doping



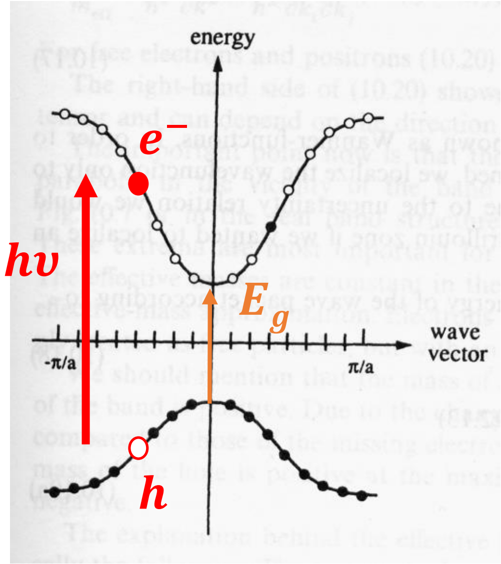
B atom → B^{-}_{fixed}+ hole



Concentration p=N_A density of dopants

Interaction of light with matter

Absorption



Incident photon

$$E = h\upsilon$$

$$K = \frac{2\pi}{\lambda}$$

* Energy conservation in the transition

$$\boxed{E_c(k_f) = E_v(k_i) + \text{h}\nu}$$

$$\Rightarrow \text{h}\nu = E_g + \frac{\hbar^2 k^2}{2}\left(\frac{1}{m_c} + \frac{1}{m_v}\right)$$

Reduced effective mass $\frac{1}{\mu} = \frac{1}{m_c} + \frac{1}{m_v}$

Ex: GaAs: m_c~$0.066m_0$; m_v~$0.4m_0$ → μ ~ $0.057m_0$ ~ m_c

* Momentum conservation in the transition

$$\boxed{\overrightarrow{k_f} = \overrightarrow{k_i} + \vec{K}}$$

Order of magnitude:
- Photons (UV - visible - near IR): K=2π/λ ~ 10^4 to 10^6 cm^{-1}
- Electrons: in the Brillouin zone, k=2π/a ~ 10^8 cm^{-1}

Ex: GaAs: a~2.8 Å

K wave vector of photon negligible → **Vertical optical transitions**

Only applies to direct bandgap SC

Absorption

Optical transition (Absorption) Rate for a photon of energy hν **=** E_c - E_v per time unit [s^{-1}]

$$R_{abs}(h\nu) = B_{vc}.\rho_j(h\nu).f_v(E_v).(1 - f_c(E_c))$$

Einstein coefficient	Density of electronic states at energy *hν*	Probability that **valence** state is occupied	Probability that **conduction** state is empty

Einstein coefficient

- * Calculated from perturbation theory: *2 discrete states 'perturbed' by a light wave*
- * **Perturbation:** Interaction electron ⇔ e.m. wave $W(t) = - q\vec{E}(\vec{r},t)\hat{r}$

  $\hat{r}$ position operator
  q electron charge

  Electric dipole Hamiltonian, see Cohen Tannoudji Ch. A_{XIII}
- * **Fermi's golden rule:**

$$B_{vc} = \frac{pq^2}{2\hbar}.\left|\langle Y_c(r)|E.\hat{r}|Y_v(r)\rangle\right|^2 \times d(E_c - E_v - \hbar w)$$

Coupling of Ψ_V to Ψ_C through $W(t)$

energy conservation

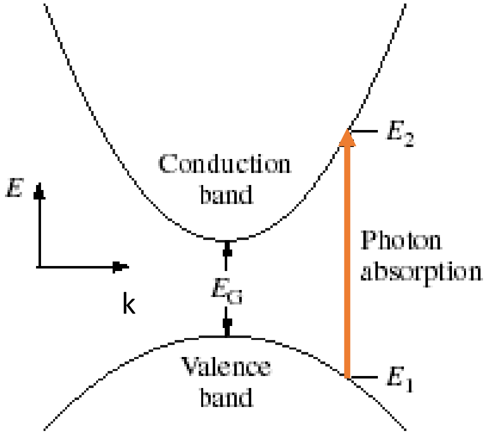
- * **Dipole matrix element**: gives strength of light-matter interaction

Absorption

Direct Absorption

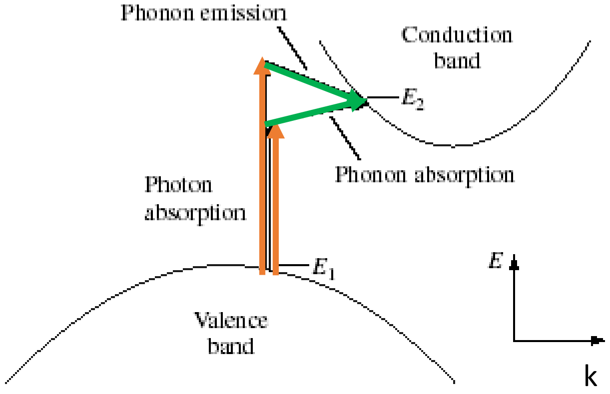
$$\alpha(h\upsilon) \approx A^*.(h\upsilon - E_g)^{1/2}$$

$$\mathrm{h\nu} = E_g + \frac{\hbar^2 k^2}{2}\left(\frac{1}{m_c} + \frac{1}{m_v}\right)$$

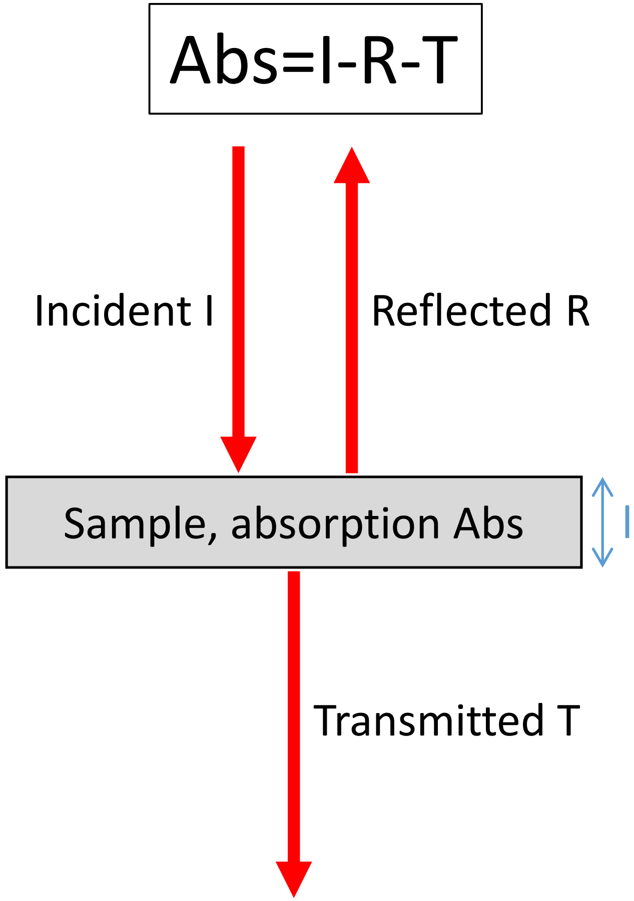


Indirect Absorption (phonons)

$$\alpha(h\upsilon) \approx \quad \alpha_a(h\upsilon) = \frac{A\left(h\upsilon - E_g + E_{phonon}\right)^2}{e^{E_{phonon}/kT} - 1} \quad + \quad \alpha_a(h\upsilon) = \frac{A\left(h\upsilon - E_g - E_{phonon}\right)^2}{e^{-E_{phonon}/kT} - 1}$$



Absorption measurement



Abs=I-R-T

Incident I

Reflected R

Sample, absorption Abs

l

Transmitted T

Absorption coeff measured by transmission of a thin platelet sample of thickness l

Beer's law $I(z) = I_0 e^{-\alpha z}$

Transmissivity of absorbing medium of thickness l

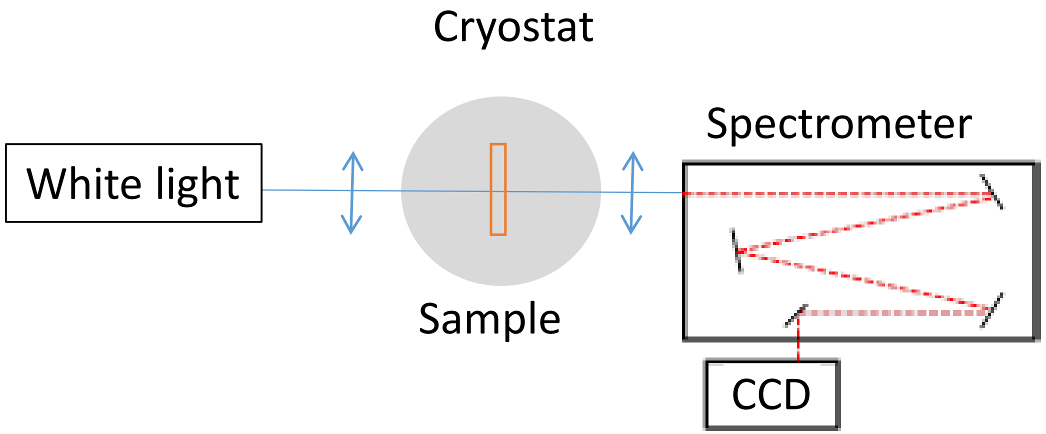
$$\boxed{T = (1-R)^2 e^{-\alpha l}} \quad \text{and} \quad \boxed{T_{\text{measured}} = \frac{I_{w/Sample}}{I_{w/oSample}}}$$

$$\Rightarrow \quad \alpha = \frac{1}{L} ln\left(\frac{I_{w/oSample}}{I_{w/Sample}}\right)$$

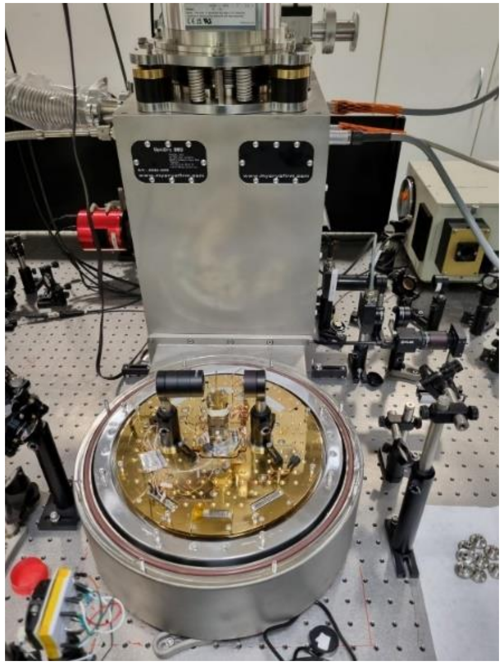
Requires transparent substrate
Requires two collection paths
Requires a reference

Absorption measurement

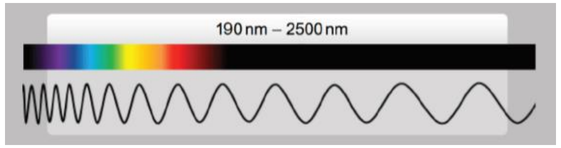
Experimental setup


Cryostat
White light
Spectrometer
Sample
CCD

Cryostat



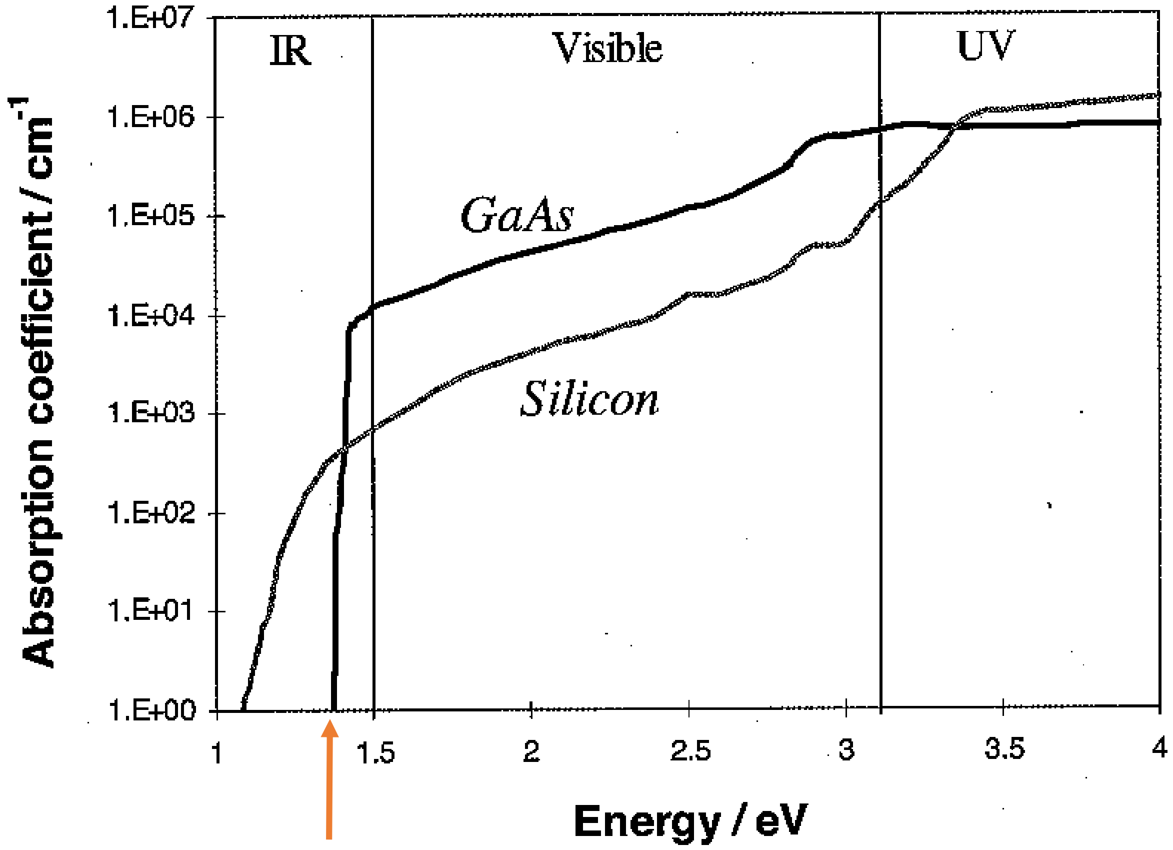
Broad wavelength range
Light source



Spectrometer

- Low excitation power
- Semiconductor choice:
  ➡ imposes choice of white lamp, mirrors/lenses, grating and detector
    - UV: PM
    - VIS: Si CCD or PD
    - NIR: InGaAs PD
- Temperature control: need for a cryostat
- Measure a reference

Absorption measurement

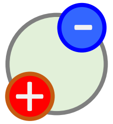


bandgap

In SC

$\alpha_{typ} \approx 10^{-4} cm^{-1}$

Excitons



Photogenerated electron AND hole are linked by coulombic interaction

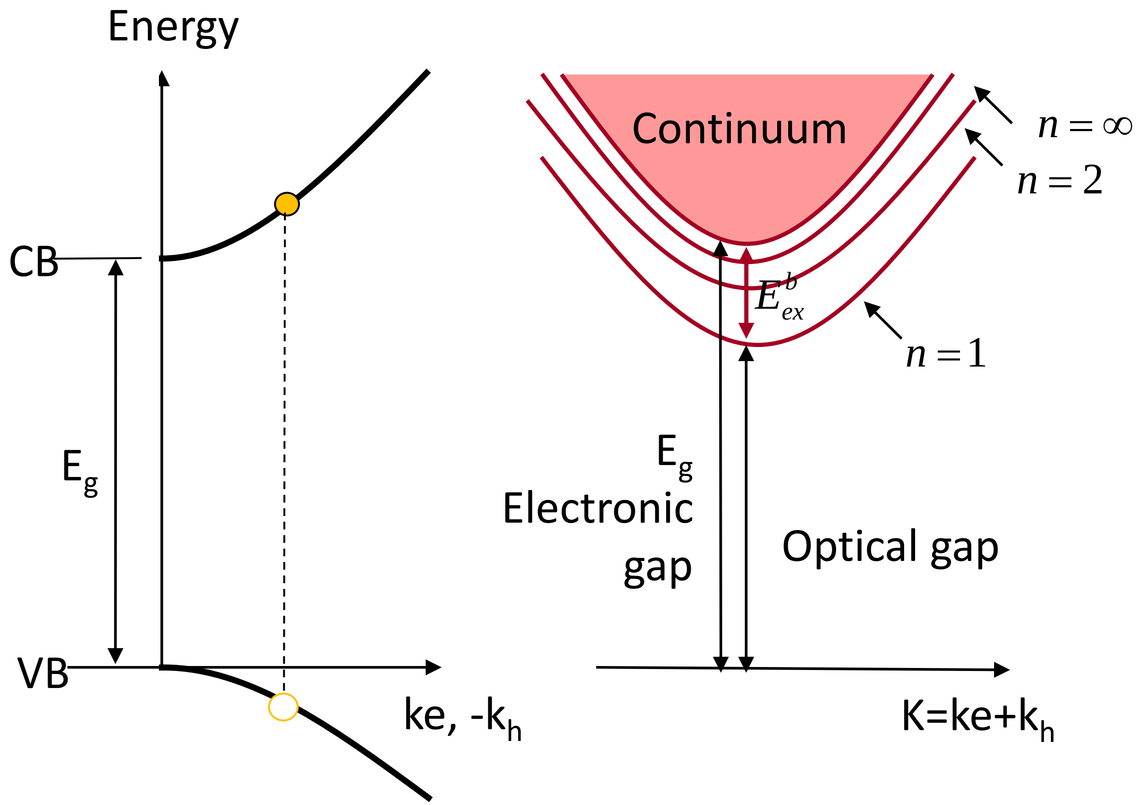
➡ **exciton**

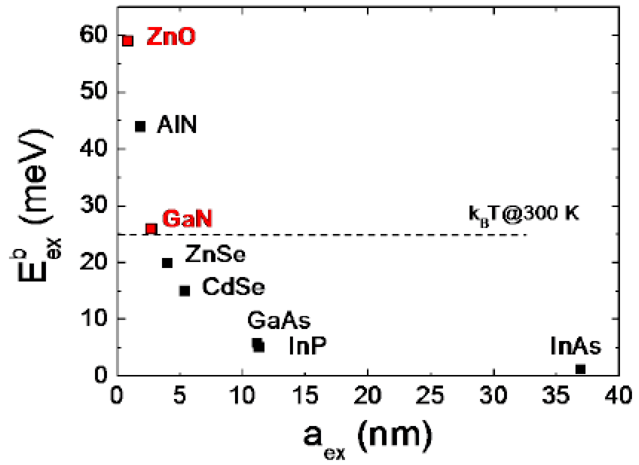
Discrete exciton energy: $E_{X,n}(k=0) = E_g - \frac{R_y^2}{n^2}$

Exciton binding energy

$$E_b^x = \frac{e^2}{2\varepsilon_0 a_B}$$

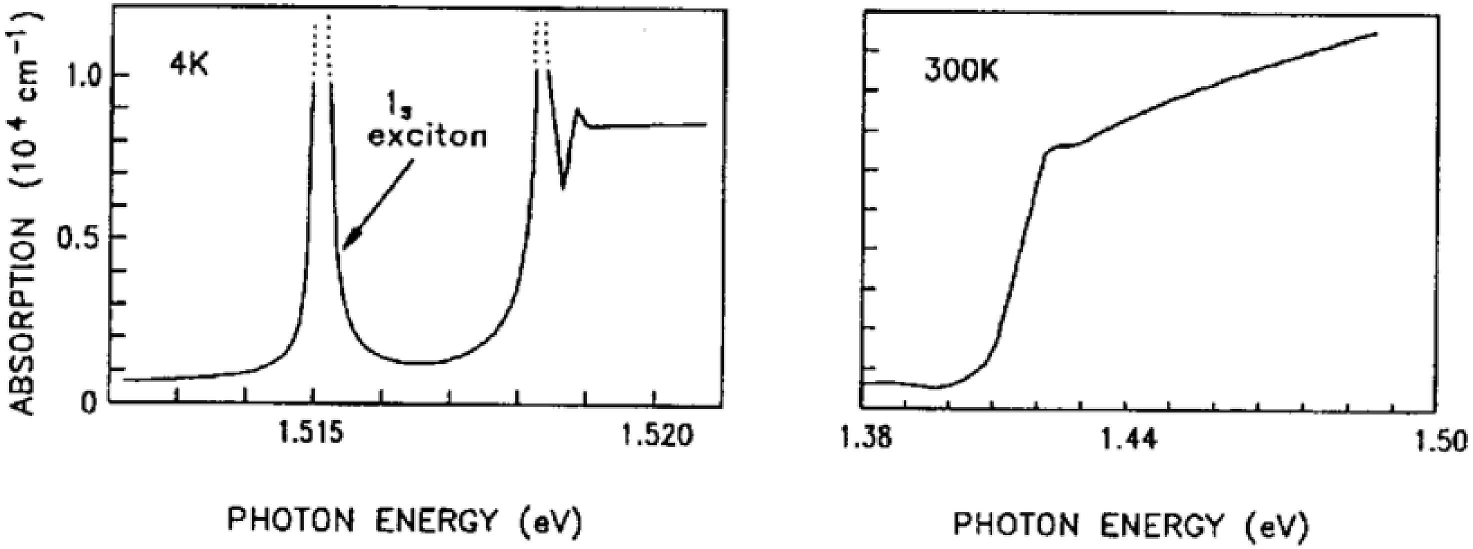
Exciton Bohr radius



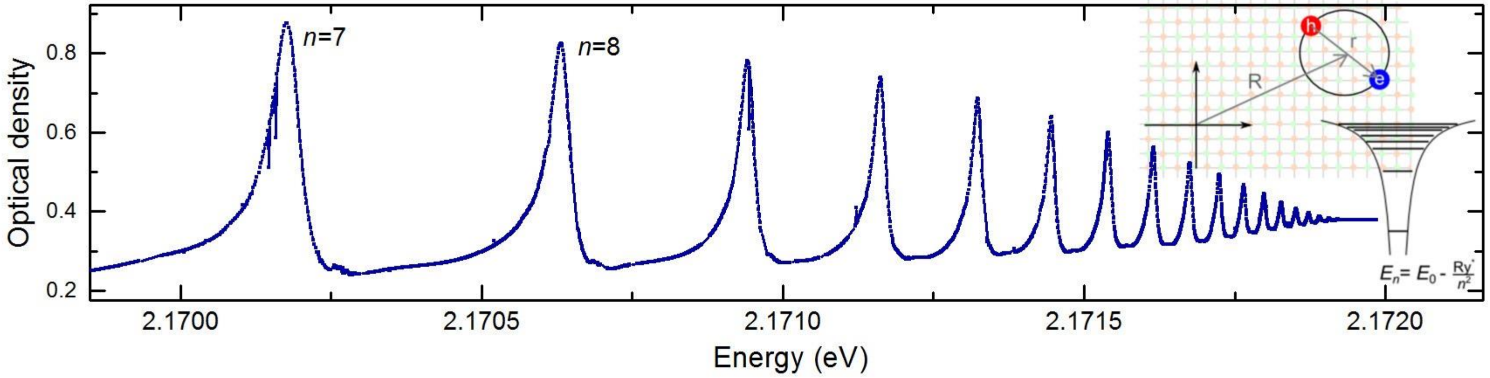


Excitons

GaAs



Cu$_2$O

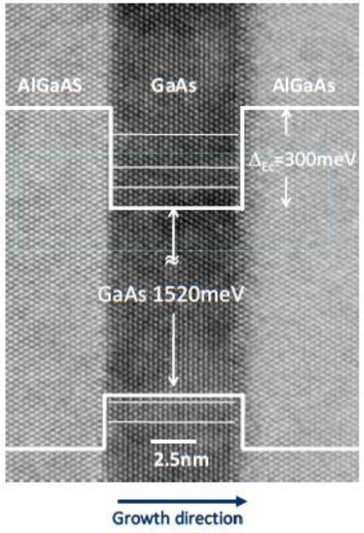


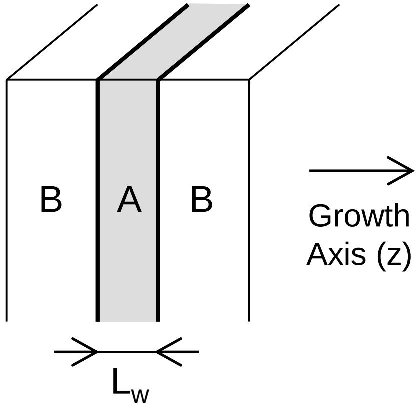
Kazimierczuk, *et al.* Nature 514.7522, 343 (2014)

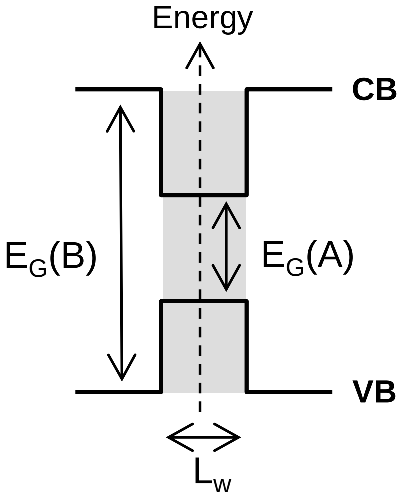
Dimensionality

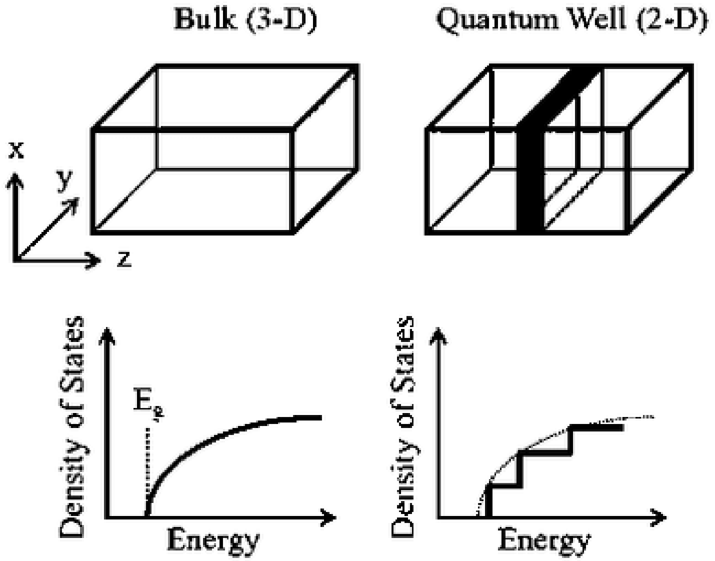
Quantum wells / 2D

Typ. L_w<few 1-10 nm

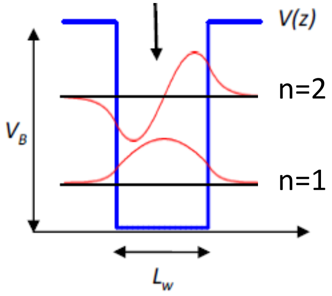








$$\Psi_i(\vec{r}) = \phi_c(z) e^{-i(k_x x + k_y y)}$$



ϕ_z	z confined
$e^{-ik_x x}$	x free
$e^{-ik_y y}$	y free

$$E_{n,k} = E_n + \frac{\hbar^2 k_\parallel^2}{2m^*}$$

Optical transitions in 2D

Same approach as in 3D: time dependent perturbation theory

calculate absorption rate $R^{abs}_{v,j\to c,i}(h\upsilon)$ of photons of energy hν between heavy holes of band j in the VB → electrons of band i in the CB using Fermi's golden rule:

$$R^{abs}_{v,j\to c,i}(h\upsilon) \propto [\text{dipole element}]\times[\text{joint density of state}]\times[\text{occupation probability}]$$

$$R^{abs}_{v,j\to c,i}(h\upsilon) = \frac{\pi}{2\hbar}\boxed{\left|\left\langle \Psi_c^i \middle| q\vec{E}_{em}\hat{r} \middle| \Psi_v^j \right\rangle\right|^2}\cdot \frac{\mu}{\pi\hbar^2}\cdot f_v^j(E_v)\cdot\left[1-f_c^i(E_c)\right] \qquad [\mathrm{s^{-1}\cdot cm^{-2}}]$$

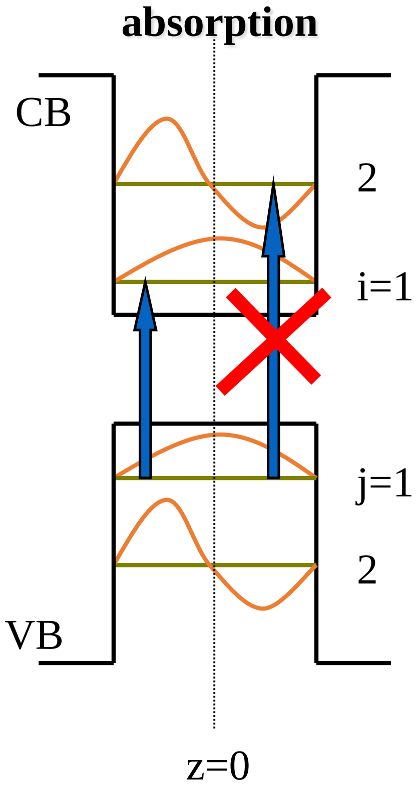
for k=0 $\quad \mathrm{Y}_c^i(k_{//}=0) = F_c^i(z)u_c(r)$

envelope function

$$\left|\left\langle \mathrm{Y}_c^i \middle| q\vec{E}_{em}\hat{r} \middle| \mathrm{Y}_v^j \right\rangle\right|^2 \ \mu\ \underbrace{\left|\left\langle u_c \middle| \vec{E}\times\hat{r} \middle| u_v \right\rangle\right|^2}_{\text{Selection rule n° 2}} \ ´\ \underbrace{\left|\left\langle F_c^i \middle| F_v^j \right\rangle\right|^2}_{\text{Selection rule n° 1}}$$

Optical transitions in 2D

envelope function $$\left|\left\langle Y_c^i \middle| q\vec{E}_{em}\hat{r} \middle| Y_v^j \right\rangle\right|^2 \mu \left|\left\langle u_c \middle| \vec{E}\times\hat{r} \middle| u_v \right\rangle\right|^2 ´ \left|\left\langle F_c^i \middle| F_v^j \right\rangle\right|^2$$



Selection rule n° 1

overlap integral of envelope functions

Selection rule n° 2:

Polarization of emission

if i (or j) is **<u>even</u>**, the envelope function is **<u>even</u>**,
if i (or j) is **<u>odd</u>**, the envelope function is **<u>odd</u>**

Hence, if (i+j) is odd ➡ $\left\langle F_c^i \middle| F_v^j \right\rangle = 0$

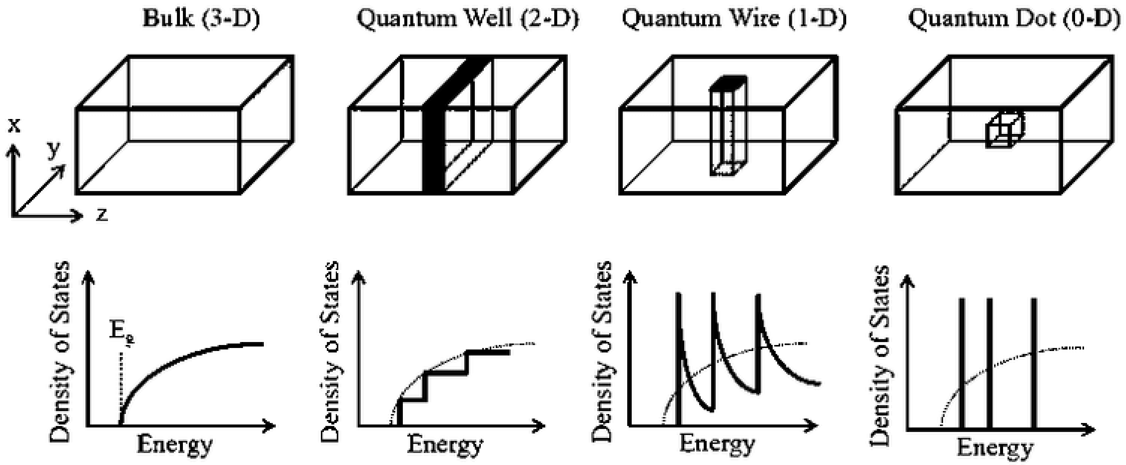
Transition is forbidden

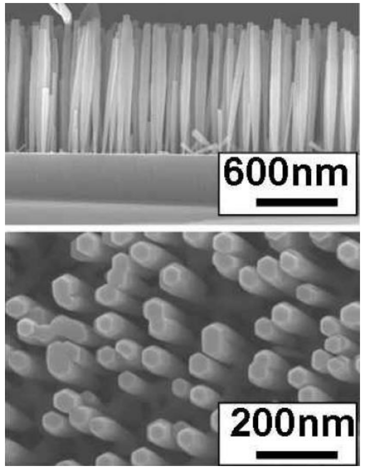
Dimensionality

Quantum wells / 2D $\Psi_i(\vec{r}) = \phi_c(z)e^{-i(k_x x+k_y y)}$

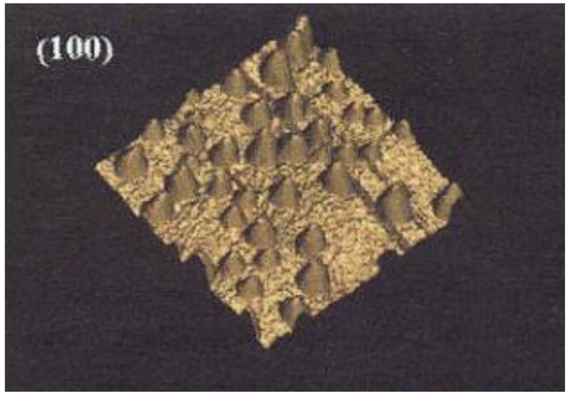
1D $\Psi_i(\vec{r}) = \phi_c(y,z)e^{-ik_x x}$

Quantum dots $\Psi_i(\vec{r}) = \phi_c(x,y,z)$





GaN nanowires



InAs Quantum dots

Outline

Basics of SC physics

* SC band structure
Density of states
Doping

* Interaction with light

* Dimensionality

Optical characterization of SC structures

* Absorption
* Photoemission

* Reflectivity

* Photoluminescence (PL)
– PL Eexcitation (PLE)

* Time-Resolved PL
– TR-Cathodoluminescence

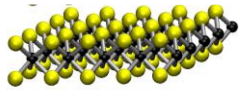
Electric/Optical characterization of SC structures

* Electroluminescence (EL)
* Photocurrent (PC)

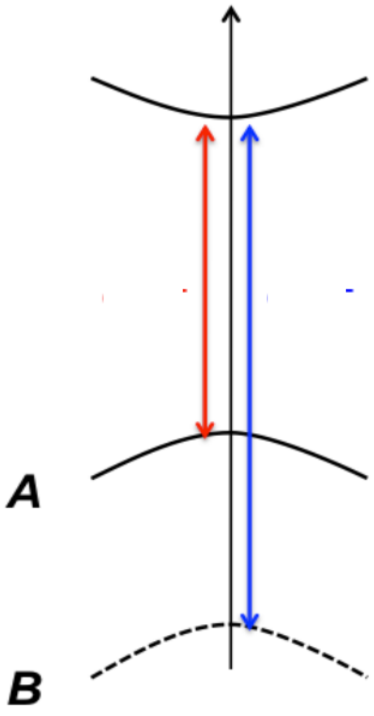
Raman spectroscopy

Absorption

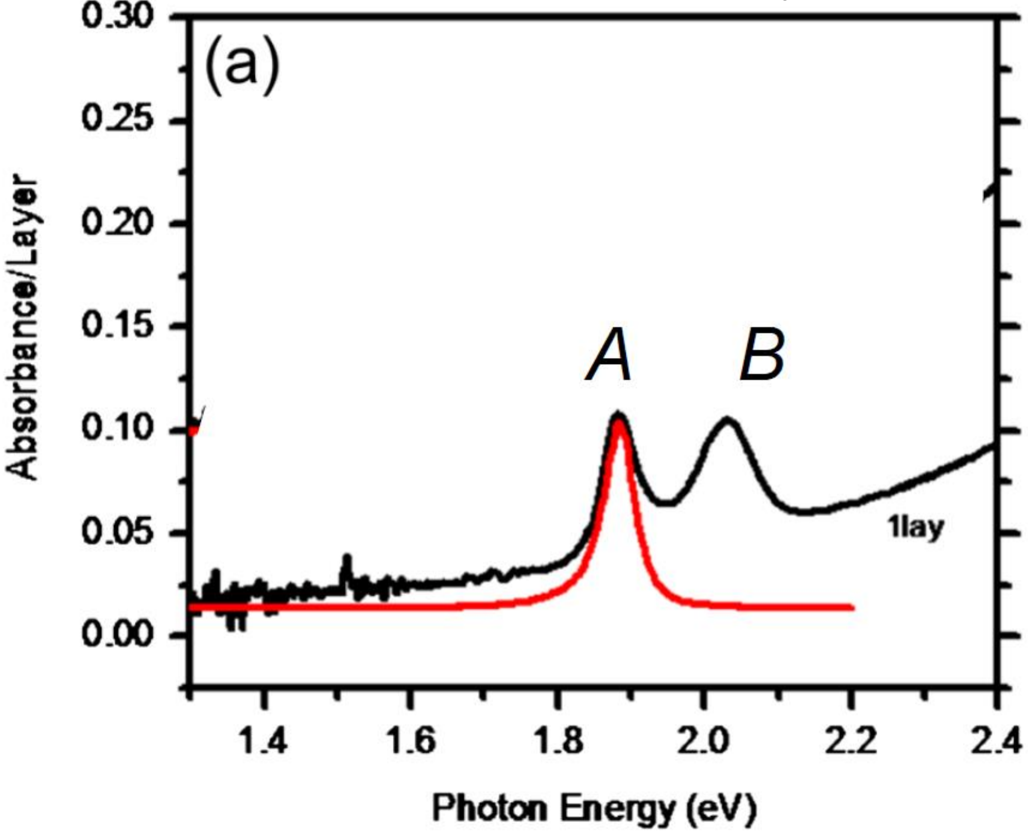
Ex:TMDC



MoS_2 monolayer



Absorption ~10 %



Phys. Rev. Lett. 105, 136805 (2010)

Photoemission Spectroscopy (UPS & ARPES)

Photoemission

* based on the **photoelectric effect**:
Photons are absorbed and electrons are ejected above vacuum level $h\nu > E_F + \phi$

* need for highly energetic photon source (typ. UV rays or He, Ar, Xe gas discharge lamp)

* Only for surface characterization: short escape depth of the photoelectrons to the surface (<10nm)

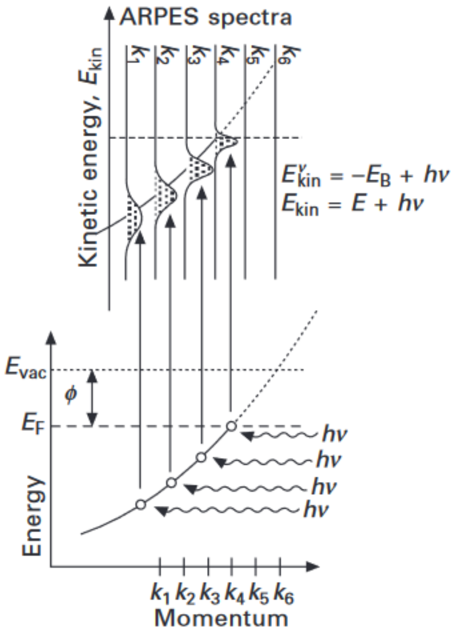
* Direct way to measure the electronic density of states near E_F (for SC: electrons in top VB)

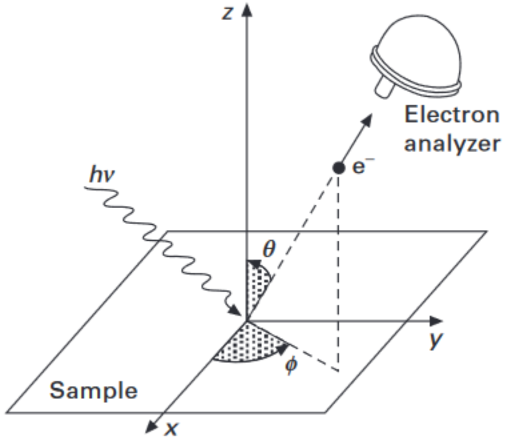
UPS : UV Photoemission Spectroscopy

ARPES: Angle resolved Photoemission Spectroscopy

Energy conservation → measurement of electron energy in the VB band

Momentum conservation → measurement of quasimomentum of the electron in the initial state given by the measurement of the photoelectron momentum



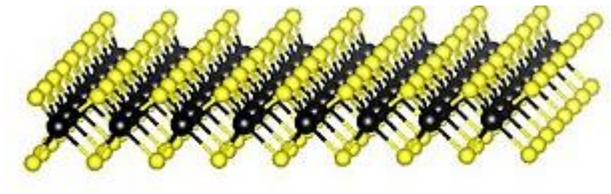


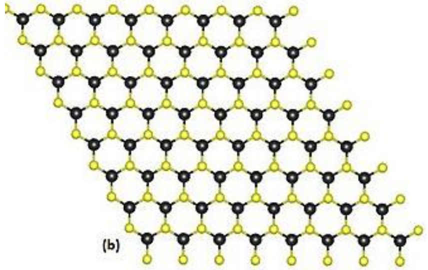
In-situ Charac. of thin film Growth 55 (2011)
Nature Reviews 2, 54 (2022)

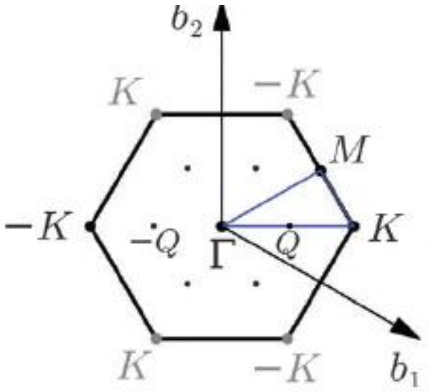
Photoemission Spectroscopy (ARPES)

Band structure of TMDC

MoSe2 - ML



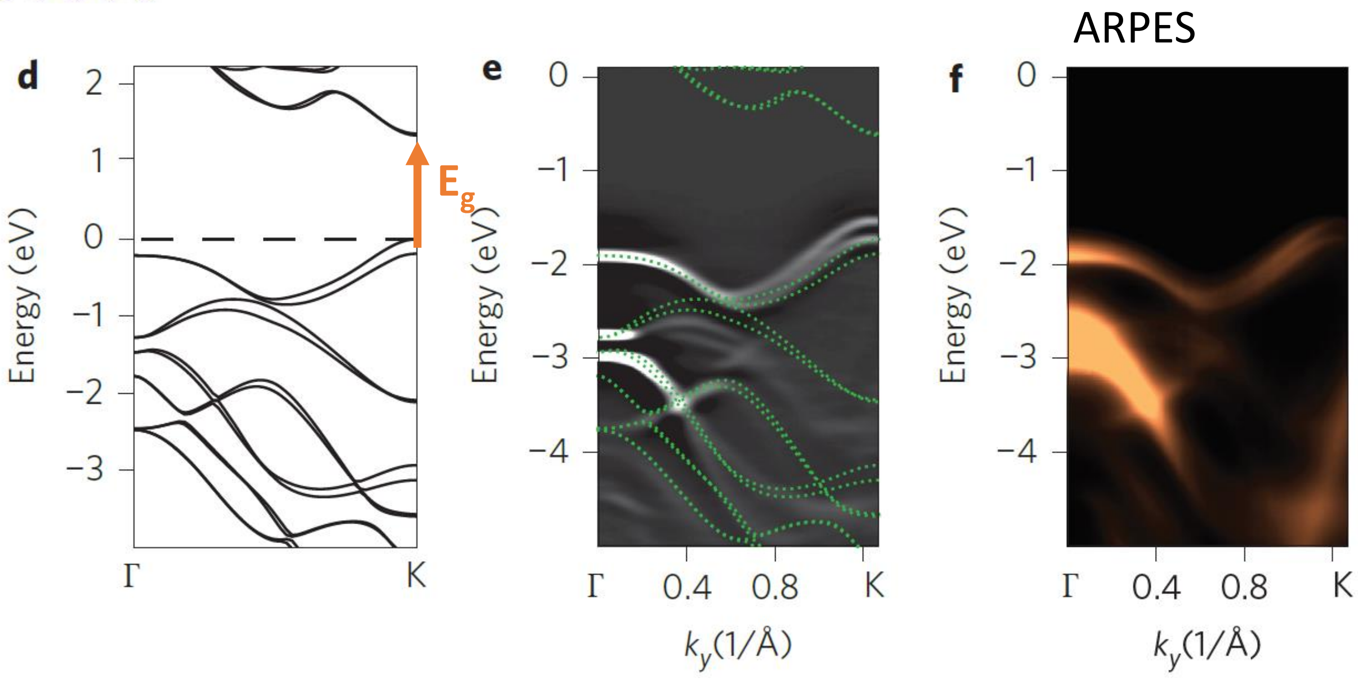




First Brillouin zone

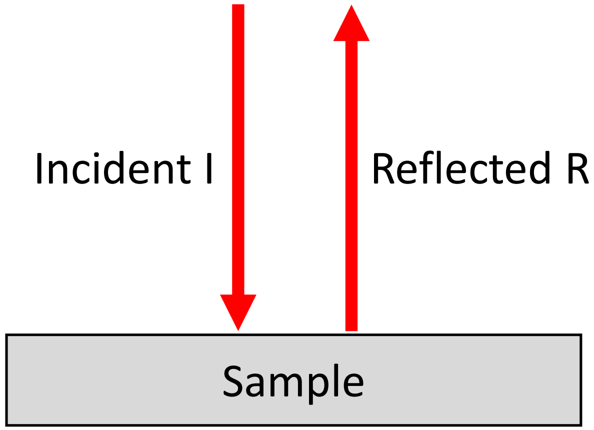
Tight-binding / k.p / DFT-GW calculations

PRB **79**, 115409 (2009), Nancy
PRB **85**, 205302 (2012), Cleveland
PRB **86**, 115409 (2012), Massachusets
2D Materials **2**, 22001 (2015), Konstanz,
…



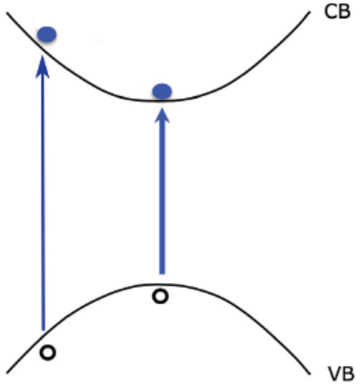
Nature Nanotechnology 9, 111 (2013)

Reflectivity



Probes vertical transitions in k-space
Probes the dielectric function

$$\varepsilon(\omega)^2 = \left(\varepsilon_1(\omega) + i\varepsilon_2(\omega)\right)^2 = \mathrm{n}(\omega) + i\kappa$$



Intensity ruled by selection rules and oscillator strength of the transition

$$\varepsilon(\omega) = 1 + \sum_k \frac{f_k}{\omega_{0,k}^2 - \omega^2 - i\omega\gamma_k}$$

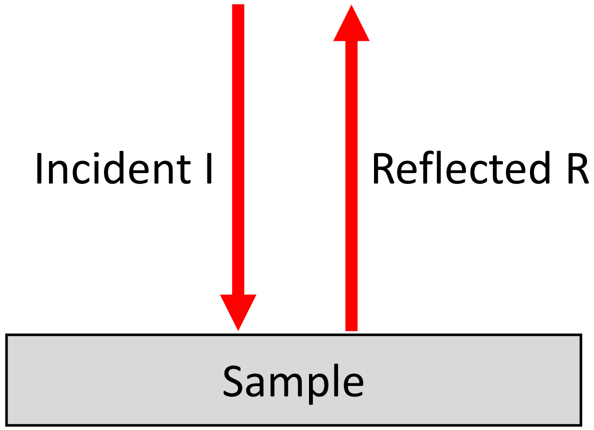
ω: incident light angular frequency
ω_0: angular frequency of the oscillator
f_k: oscillator strength of oscillator and electric field of light
γ_k: damping factor

➡ Requires a model (transfer matrix for instance) or a transformation (Kramers Kronig) to extract quantitative parameters (energy of the transition, oscillator strength, linewidth,…)

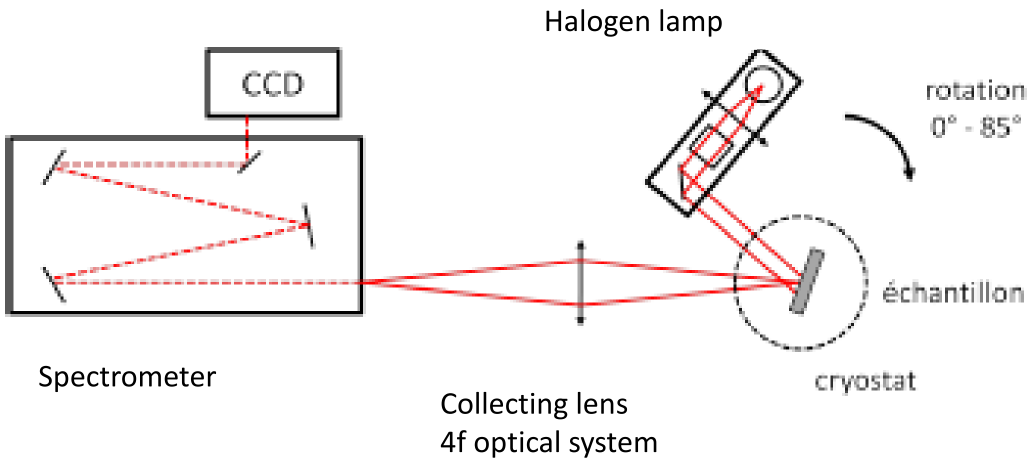
➡ Requires the precise measurement of the optical index of the sample (measured by ellipsometry for ex)

Reflectivity measurement

Experimental setup



Angle-resolved reflectivity setup



Source: white lamp (Halogen, Xe,…)

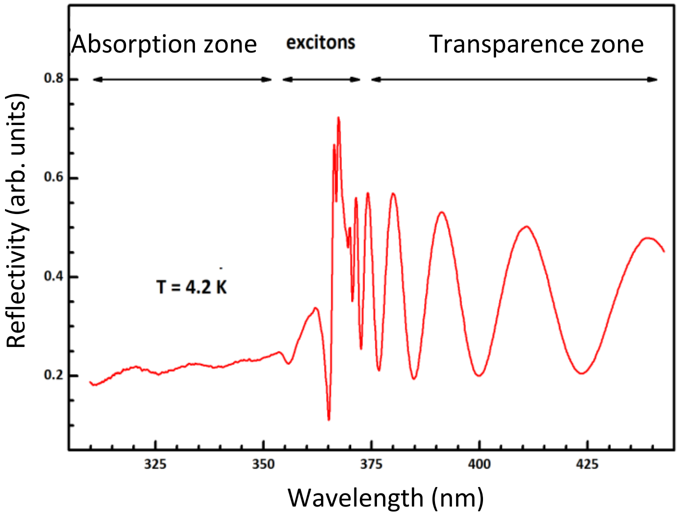
Reflected beam:

spectrally resolved using spectrometer
intensity recorded using CCD ou sCMOS camera

Reflectivity R = $\frac{I_{w/sample}}{I_{white\ lamp}}$

Reflectivity measurement

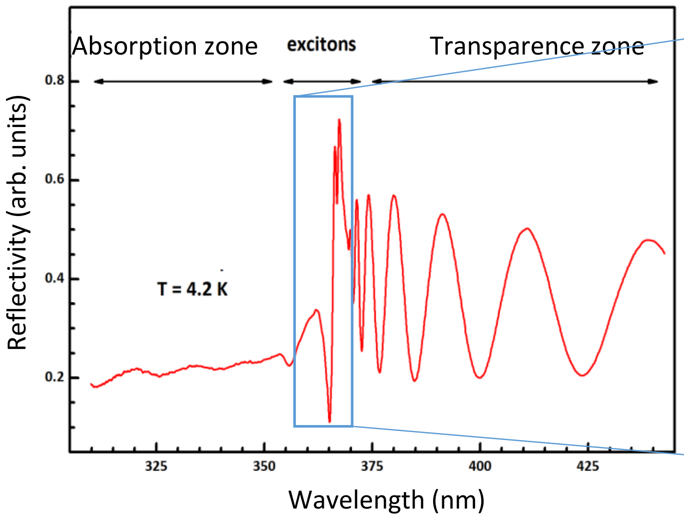
Ex: ZnO epilayer



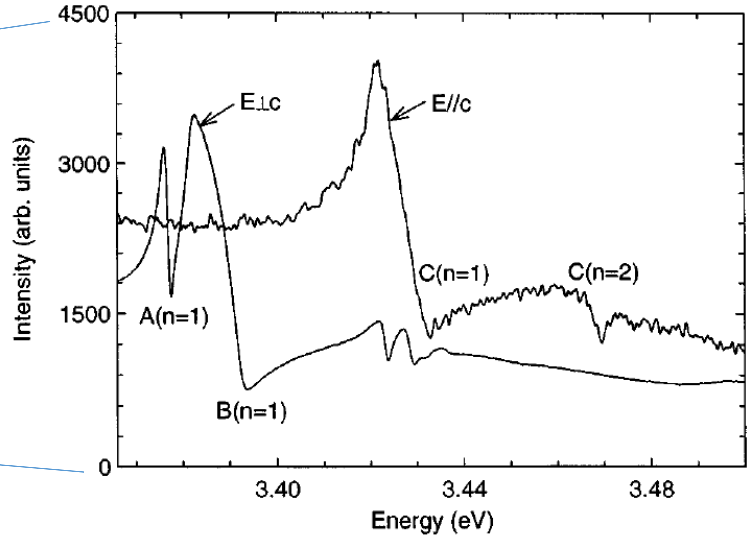
François Médard PhD thesis (2010)

Reflectivity measurement

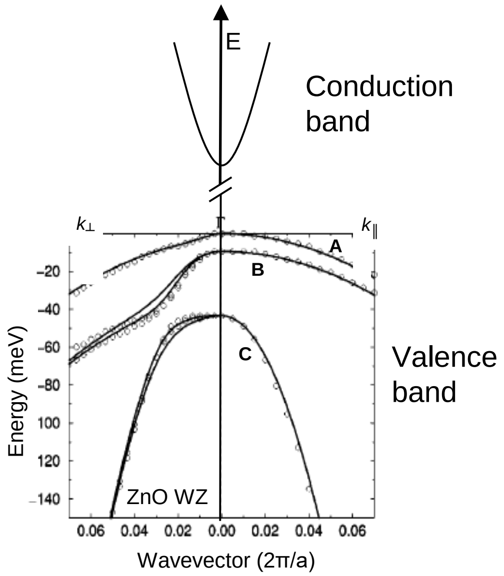
Ex: ZnO epilayer

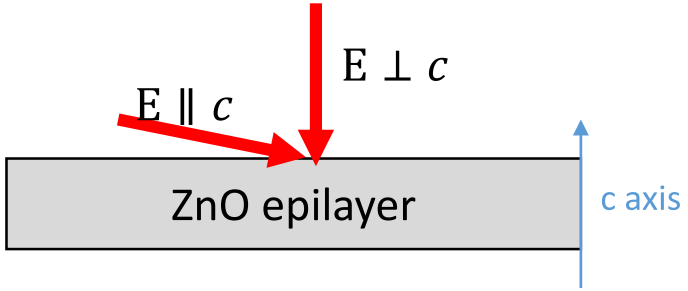


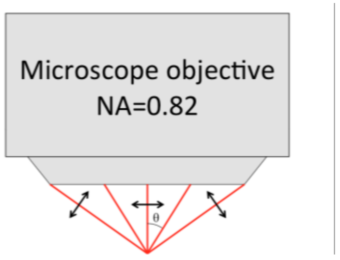
François Médard PhD thesis (2010)



Reynolds, PRB 60, 2340 (1999)







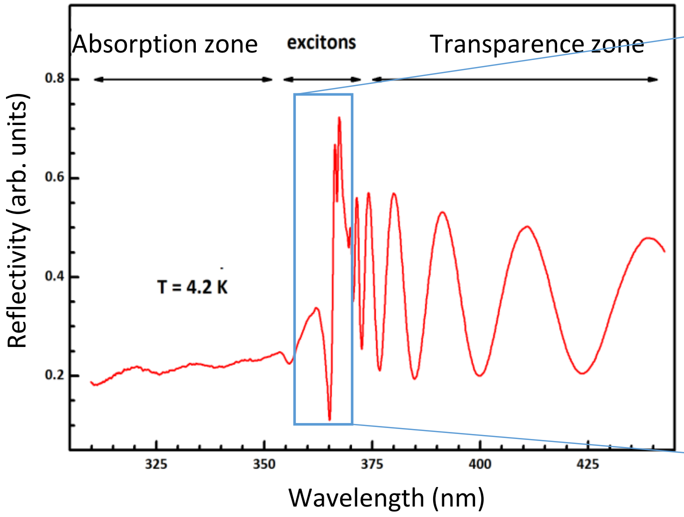
Selection rules:

A & B excitons mainly coupled to $\mathrm{E} \perp c$

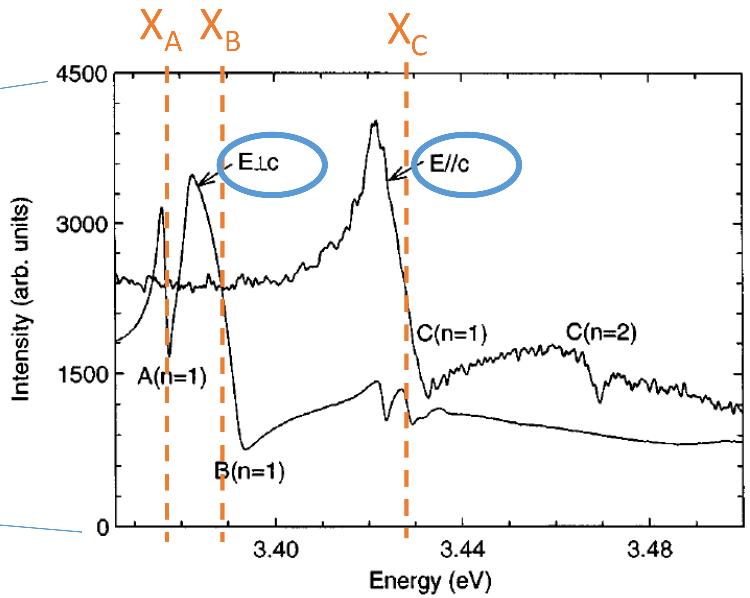
C excitons mainly coupled to $\mathrm{E} \parallel c$

Reflectivity measurement

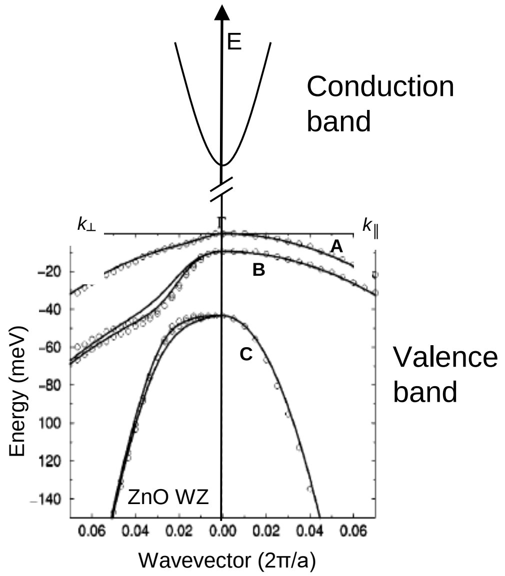
Ex: ZnO epilayer

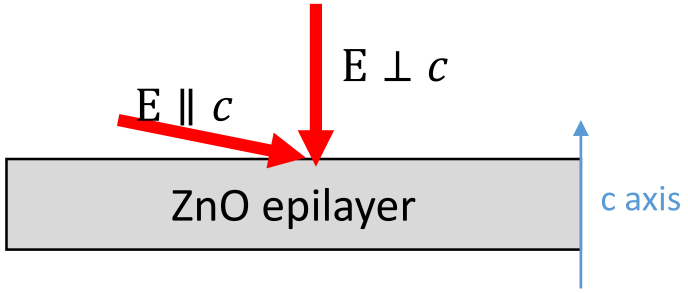


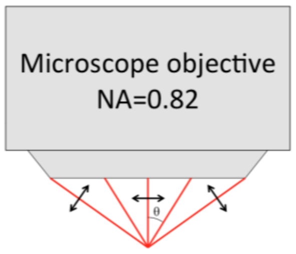
François Médard PhD thesis (2010)



Reynolds, PRB 60, 2340 (1999)







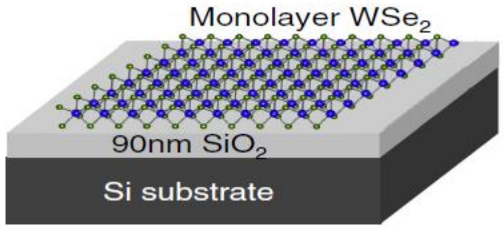
Selection rules:

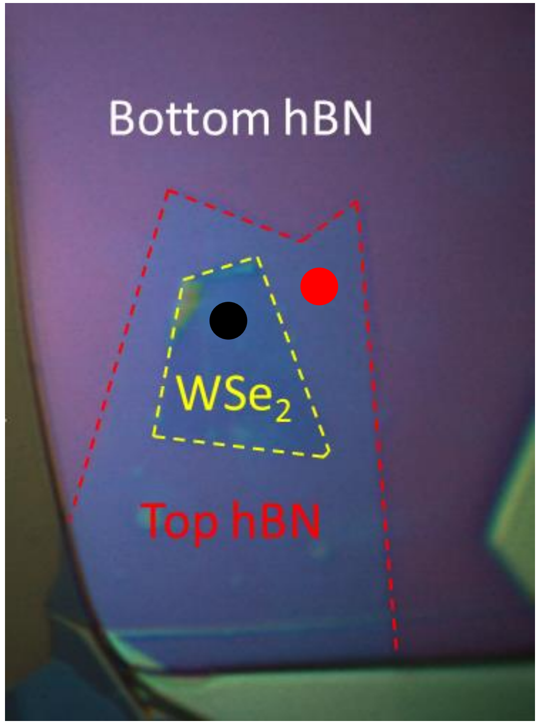
A & B excitons mainly coupled to $\mathrm{E} \perp c$

C excitons mainly coupled to $\mathrm{E} \parallel c$

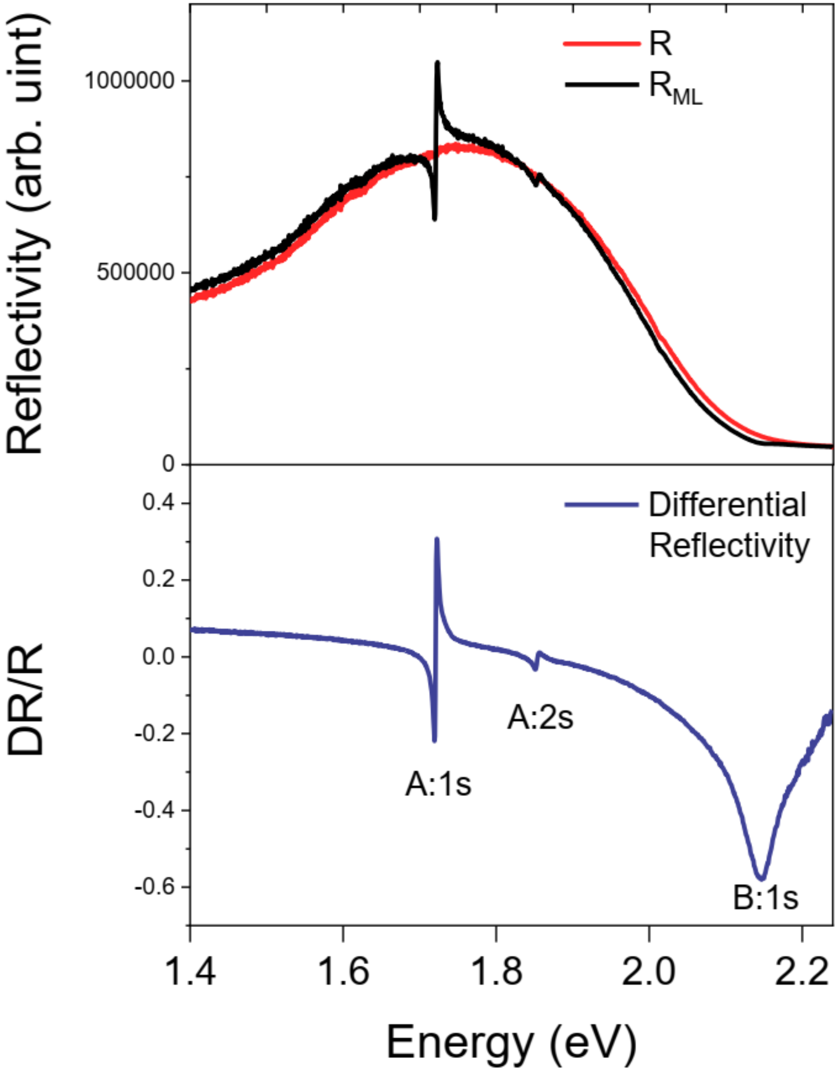
Reflectivity

Ex: WSe_2 monolayer



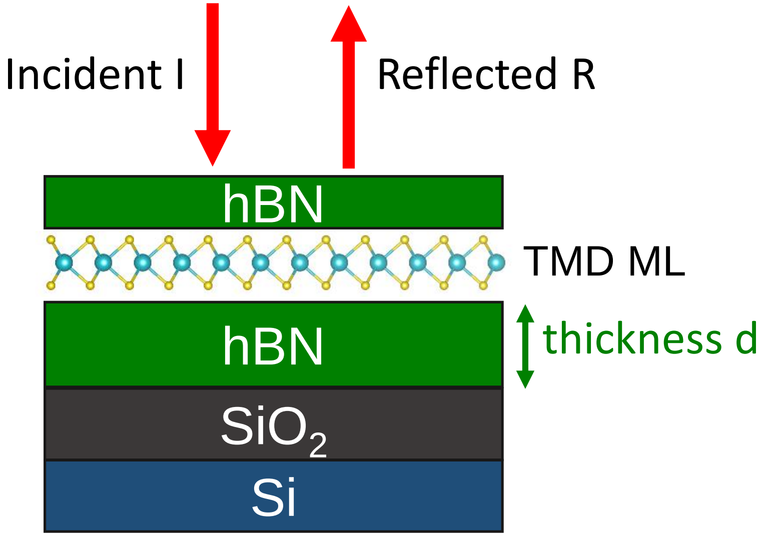


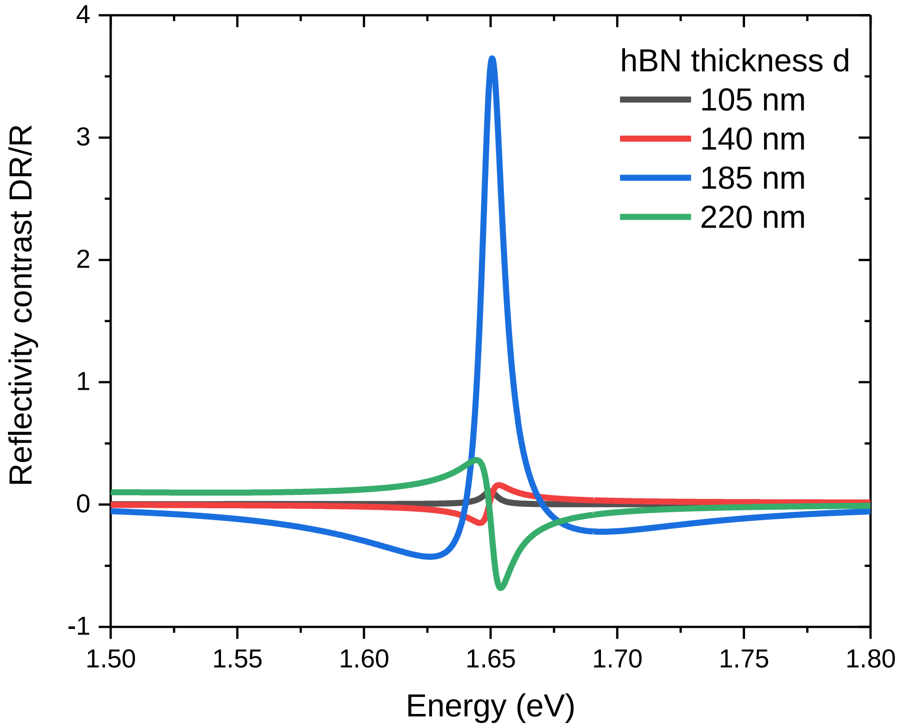
Reflectivity Contrast: $DR/R=(R_{ML}-R)/R$



Reflectivity

Ex: WSe_2 monolayer

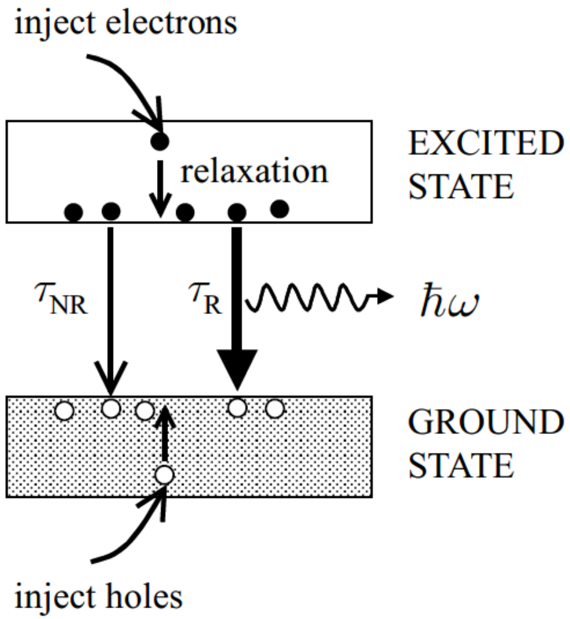




Amplitude and shape of reflectivity contrast depends on thicknesses of dielectric layers

➡ Use of transfer matrix model needed to extract quantitative parameters (energy of the transition, oscillator strength, linewidth)

Luminescence



Probes how **excess energy is released by emission of light**

Photoluminescence: the emission of light after absorbing a photon of higher energy

Electroluminescence: the emission of light caused by running an electrical current through the material

… And others (**Cathodo-**, thermo-, chemi- etc)

$$\Phi(E)=\underset{\uparrow}{|M|}^2.g(E). \quad \textit{level occupancy factor}$$

Matrix of light-mater interaction

Luminescence

Radiative recombination :

At equilibrium (no excitation – thermal emission)

$$n^0 = \int_{E_g}^{\infty} g_c(E) f_e(E) dE = N_c \exp\left(\frac{E_F - E_c}{kT}\right)$$

$$p^0 = \int_{E_g}^{\infty} g_v(E) f_h(E) dE = N_v \exp\left(-\frac{E_F - E_v}{kT}\right)$$

Fermi level

$$E_F = E_c + kT \ln\left(\frac{n}{N_c}\right) \qquad n_i^2 = n^0 p^0$$

Out of equilibrium (under excitation) - excess carrier Δn=Δp

$$n = n^0 + \Delta n = N_c \exp\left(\frac{E_{Fn} - E_c}{kT}\right)$$

$$p = p^0 + \Delta p = N_v \exp\left(-\frac{E_{Fp} - E_v}{kT}\right)$$

Quasi-Fermi levels

$$\Delta\mu = qV = E_{Fn} - E_{Fp}$$

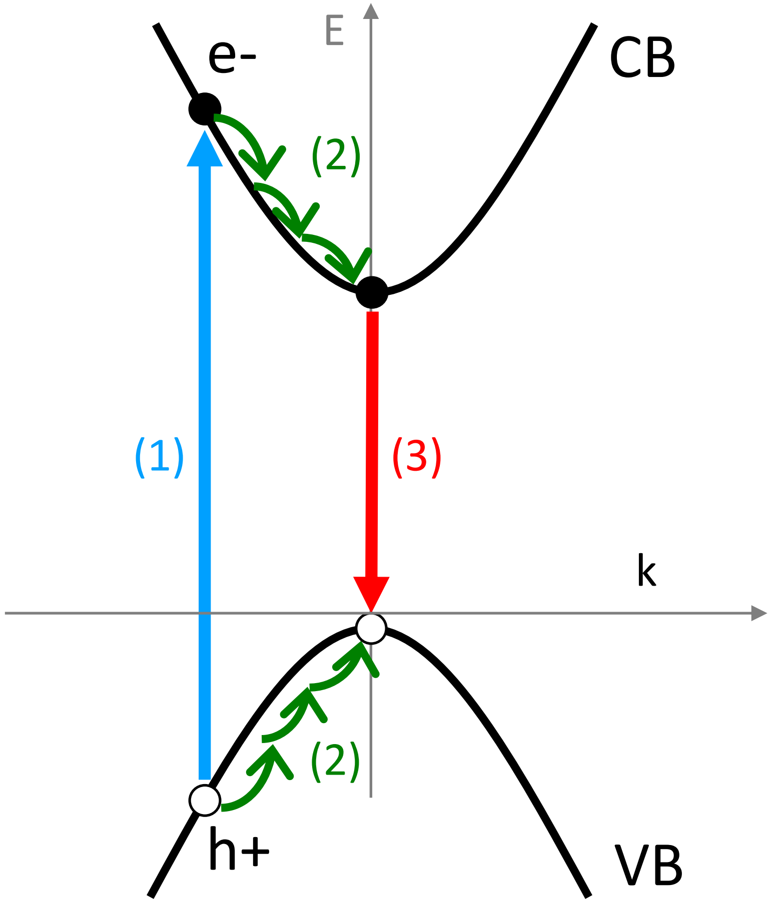
Simplified expression for recombination (out of equilibrium)

$$R = Bnp = R^0 \exp\left(\frac{E_{Fn} - E_{Fp}}{kT}\right)$$

Bimolecular recombination

Photoluminescence (PL)

a powerful tool to understand electronic structure of semiconductors



(1) absorption
- How efficient is absorption?
- Depend on which states is excited

(2) relaxation
- Many possible interactions: excitons-phonons, excitons-excitons, exciton-electrons

(3) recombination
- Depend on oscillator strength
- Depend on population of the given state
- (But not simply proportional to the density of states)
- Selection rules
- Radiative vs non radiative

Requires complementary experiments and tuning knobs

Photoluminescence (PL)

Experimental setup

- Advantages

  *No sample preparation/no contacts/no transparent substrate

  *Background free : very weak signals can be detected – to the single-photon ultimate limit

  *Fixed wavelength laser excitation is enough (Choose $E_{laser}>E_g$)

- Drawbacks

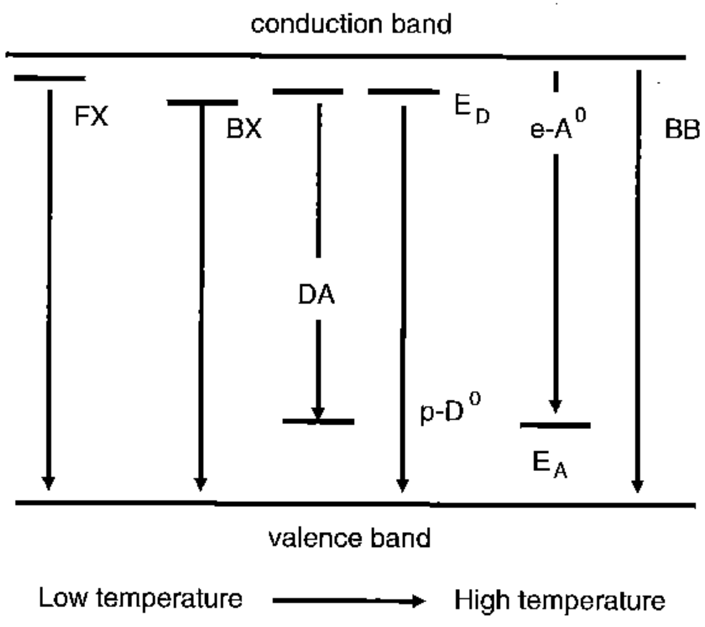
  *Requires low temperature

  *Probes **intrinsic** and **extrinsic** states (linked to defects, energy levels in the bandgap…)

  ⇨ PL is not simply proportional to density of states
  PL energy gives information on lowest states only

  *PL Intensity is affected if transitions are not radiative due to:

  - Recombination on traps or impurities (vacancies, dislocations, joint grains…)
  - Surface recombination



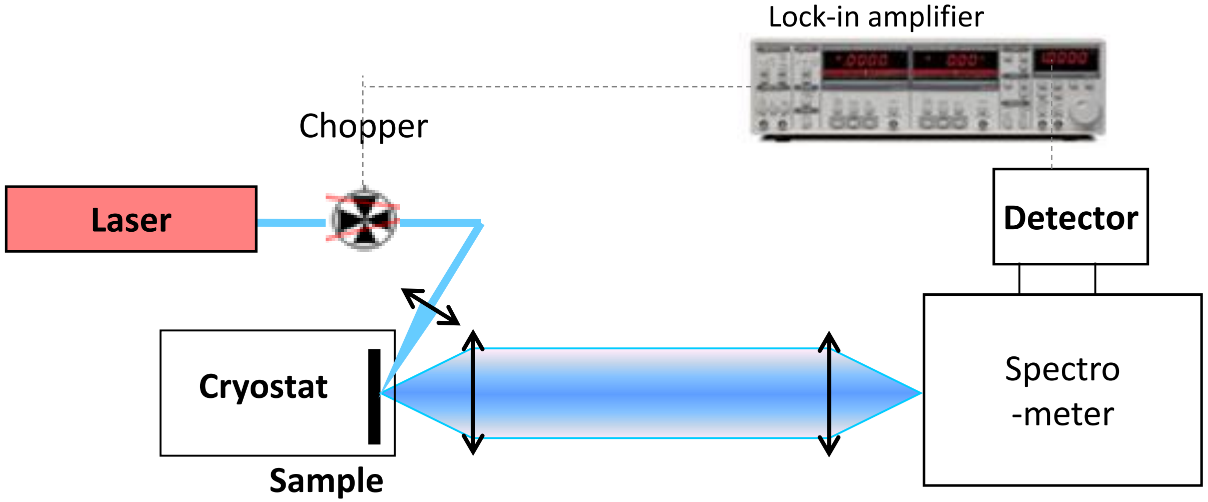
Photoluminescence (PL)

Experimental setup

*Choose E_{laser}>E_g or Tunable laser

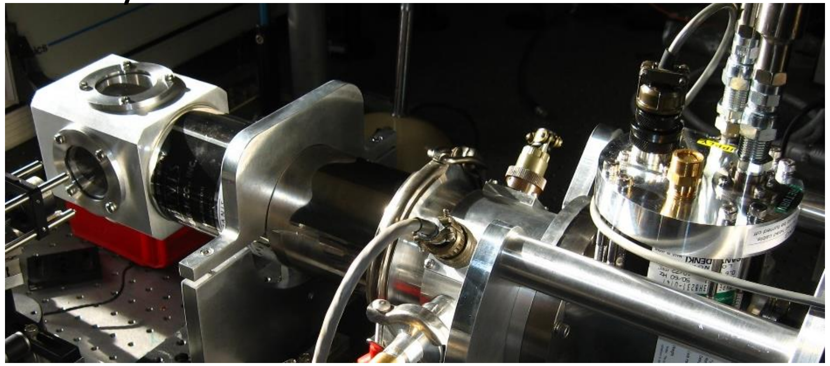
*Laser spot size = spatial resolution ~100µm

*Spectral resolution given by grating and spectrometer



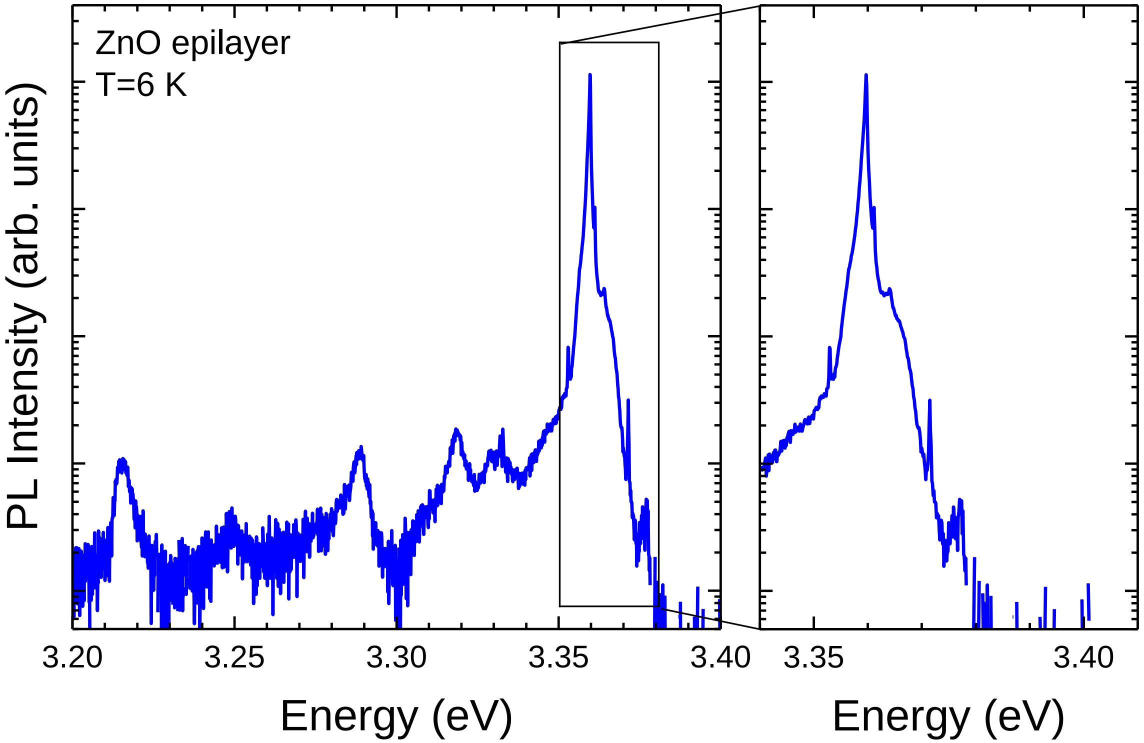
Supercontinuum laser

4K cryostat



Photoluminescence

Ex: ZnO epilayer



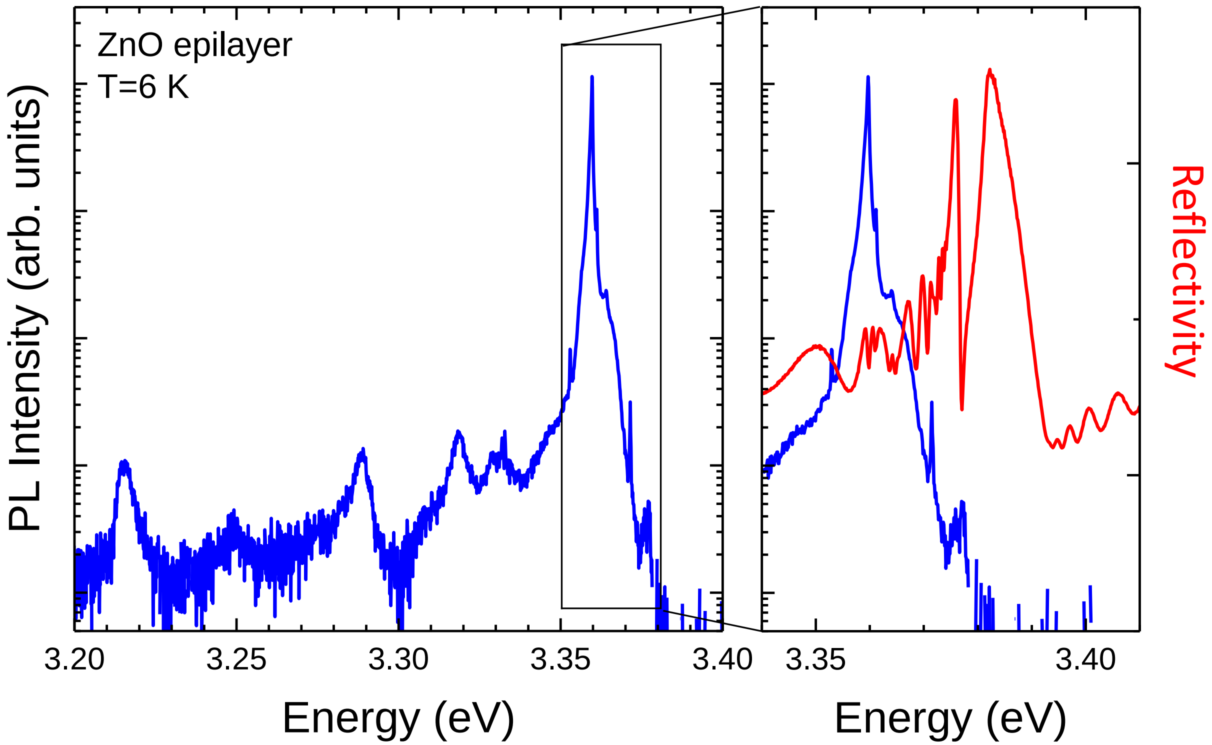
PL spectrum presents many lines !!

➡ Need for complementary experiments

Photoluminescence

Ex: ZnO epilayer

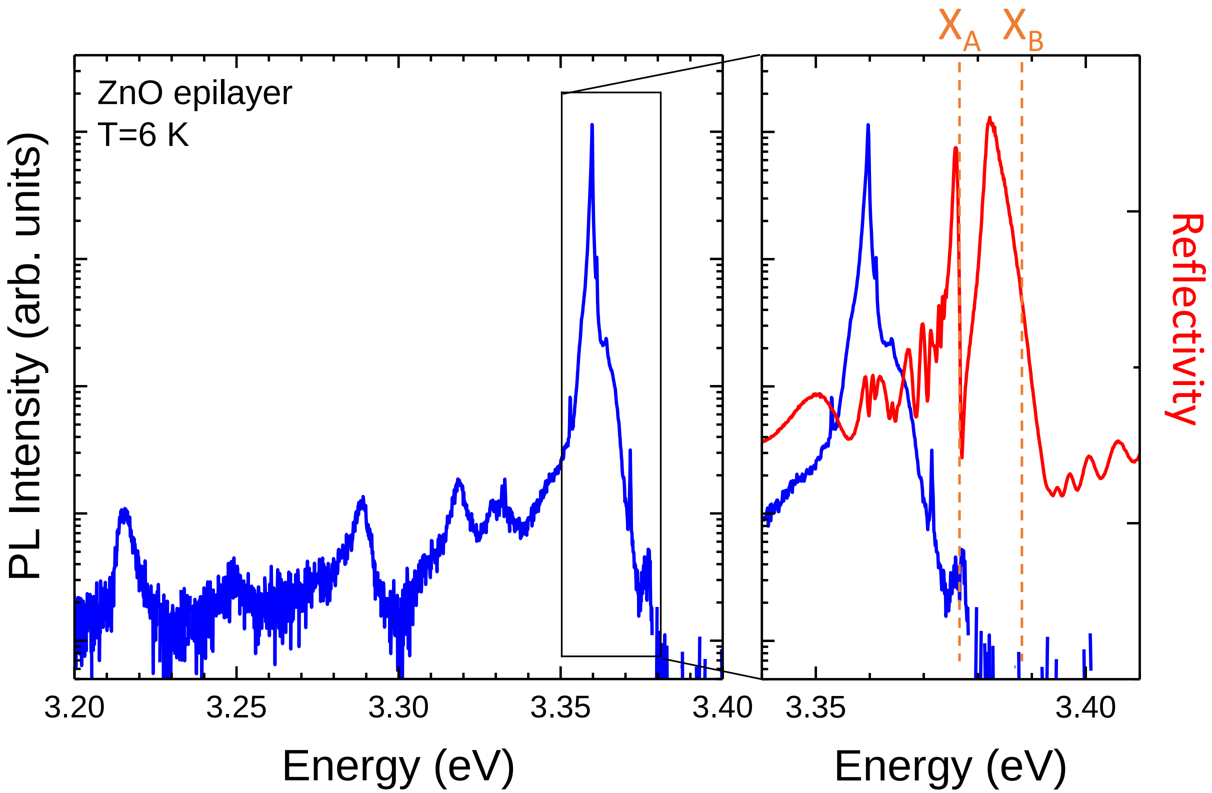
\+ Reflectivity



Photoluminescence

Ex: ZnO epilayer

+ Reflectivity



* Reflectivity reveals the free exciton lines

* PL spectrum is dominated by other lines even if oscillator strengths of free exciton transitions are strong

→ Excitonic complexes bound to donor states

Photoluminescence

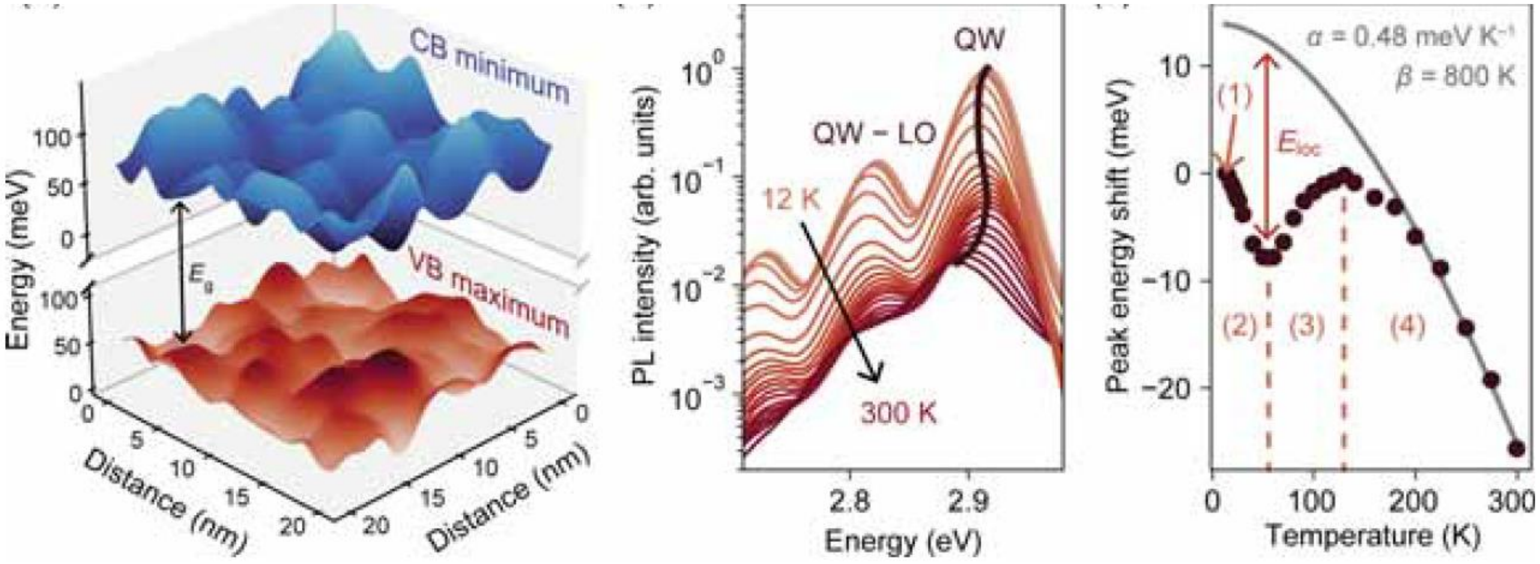
Ex: InGaN quantum wells

PL energy gives information on lowest states only
PL widths gives information on inhomogeneity

tuning knob=temperature

Random alloy disorder in InGaN QW ➡

Inhomogeneous broadening of QW PL peak
Localisation: S-shape of E=f(T)
Non radiative channels: low signal at 300 K



EFFL Thomas Weitherley PhD thesis

Varshni's law

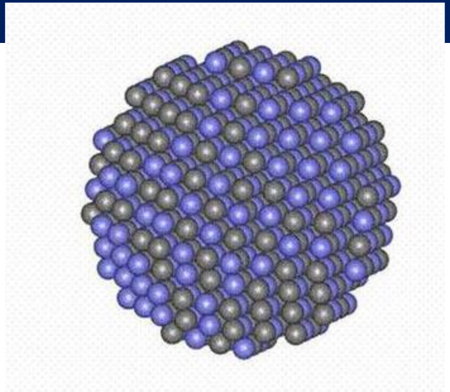
$$E_g(T) = E_g(0) - \frac{\alpha T}{T + \beta}$$

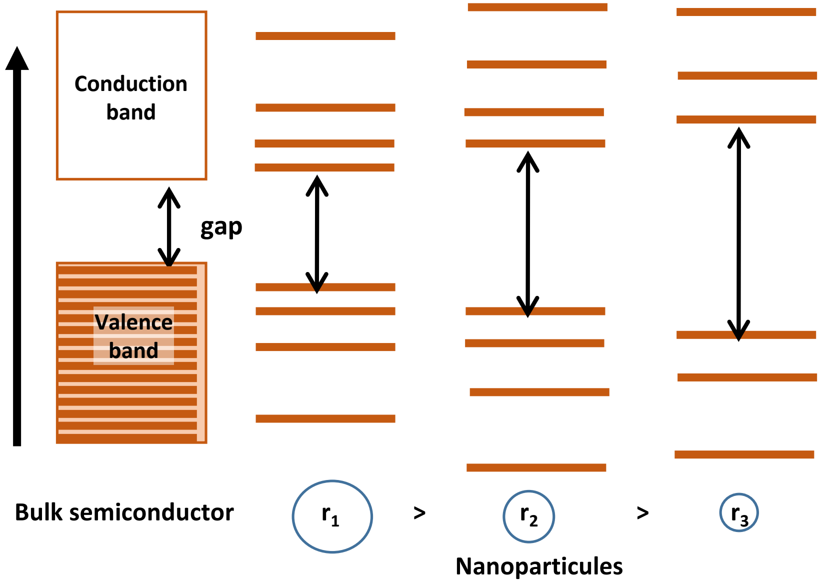
Photoluminescence

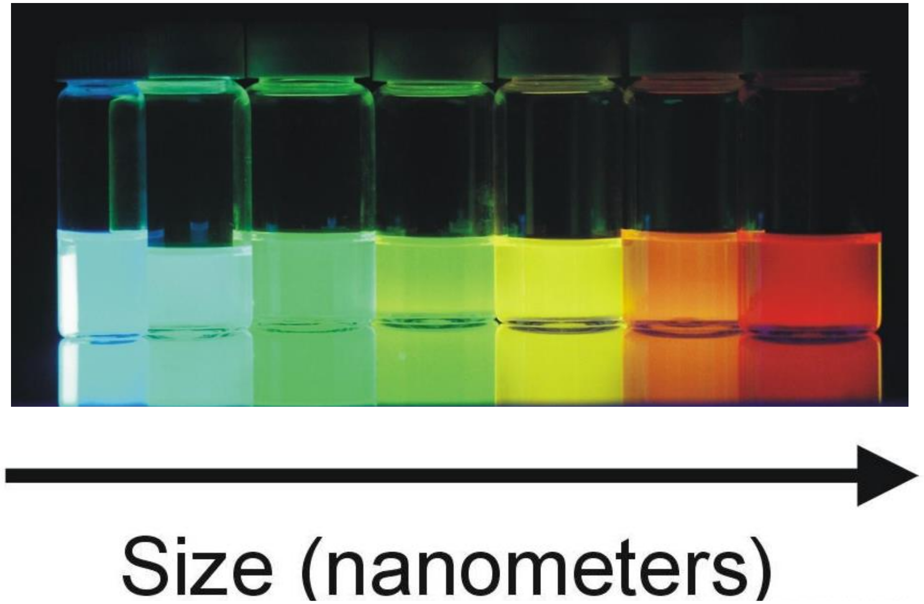
Ex: Quantum dots / Nanoparticules

Nobel prize 2023

Confinement in nanoparticules: effect on the optical properties



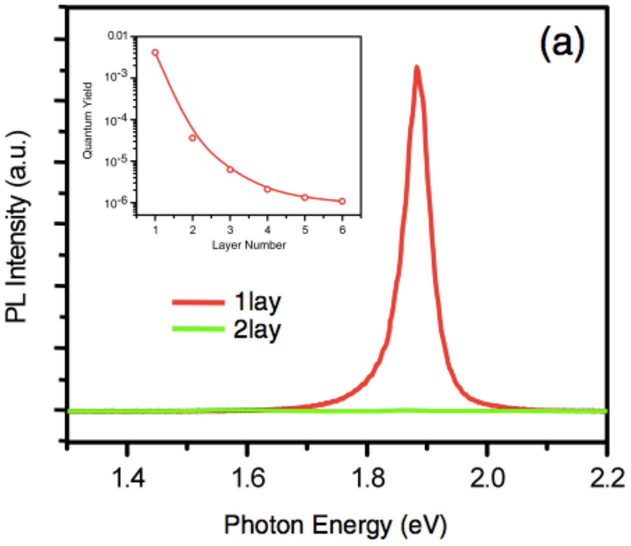


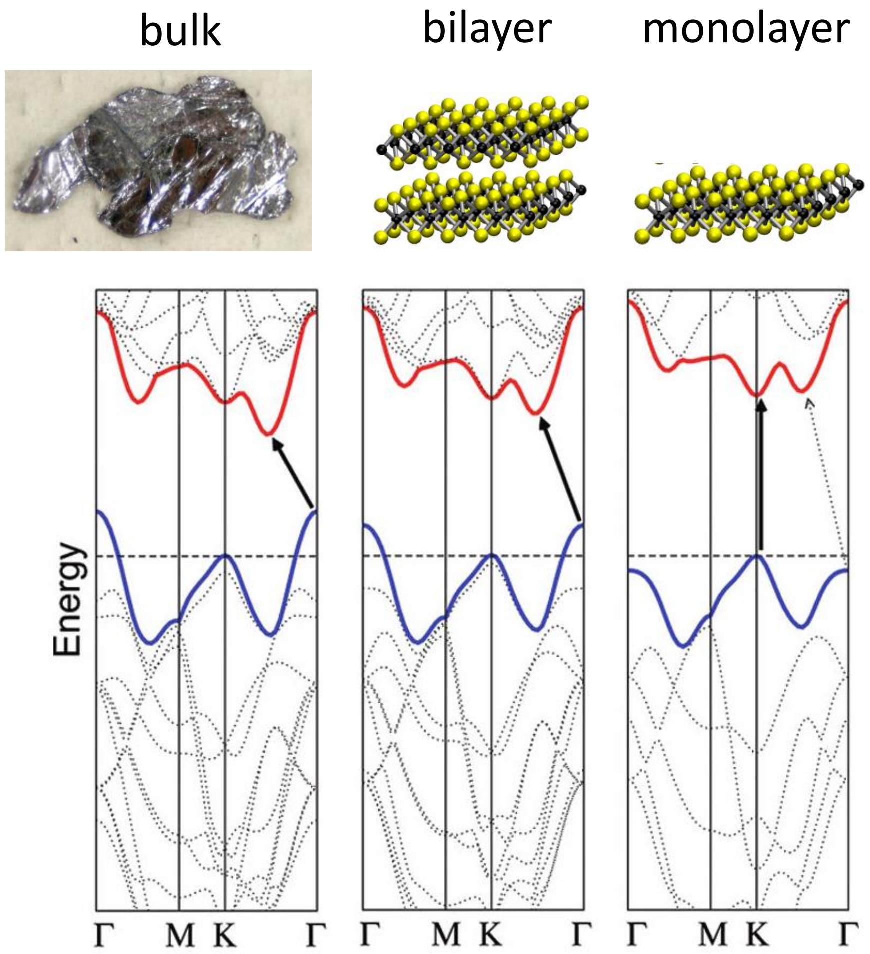


Reduction of size of NPs → increase of the energy bandgap

Photoluminescence

Ex: MoS_2



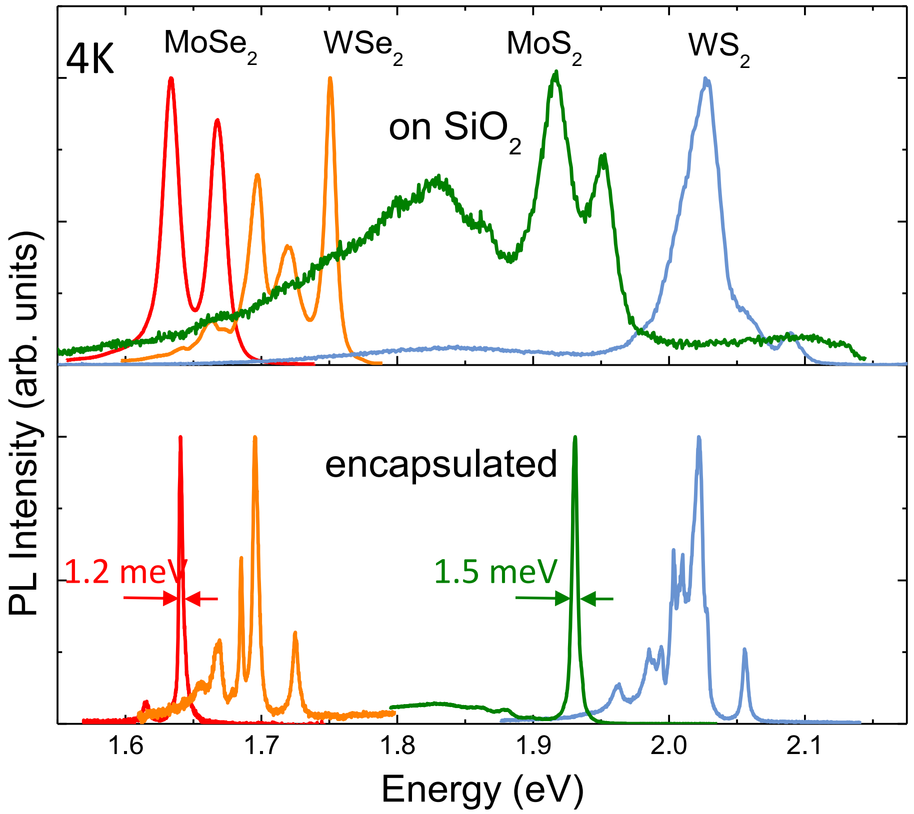


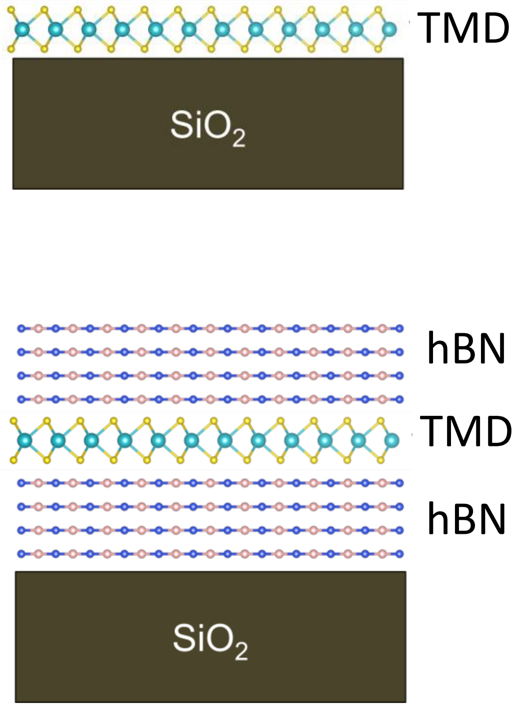
From multilayer to monolayer ➡ Indirect to direct bandgap

A. Splendiani et al. Nano Lett. 10, 1271 (2010)
B. Mak et al. Phys. Rev. Lett. 105, 136805 (2010)

Photoluminescence

Ex: TMDC





The optical quality is strongly influenced by the environment

hBN encapsulated samples →narrow transitions→limited by homogeneous linewidth

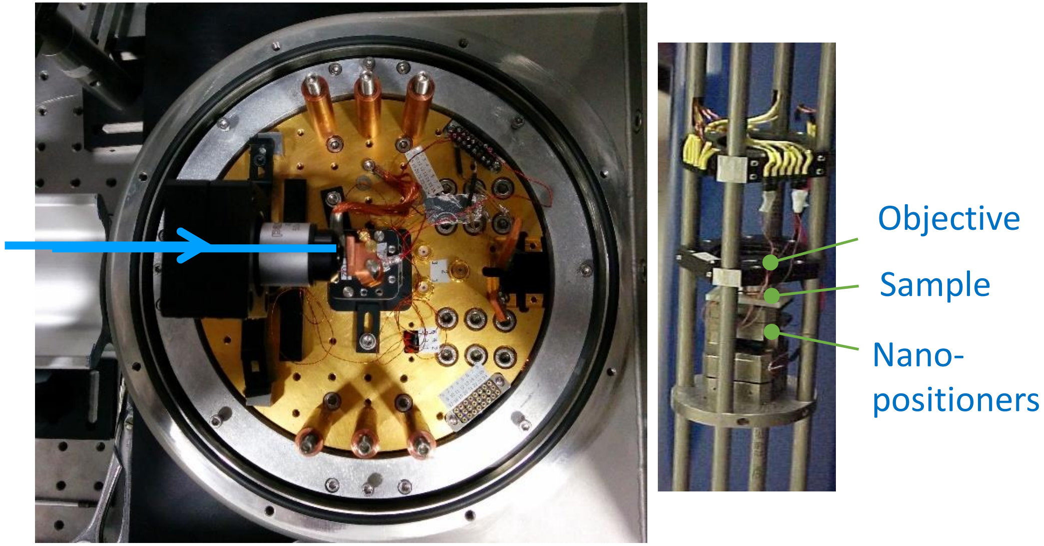
PRX 7, 021026 (2017); *2D Mater.* **4** 031011 (2017) ; arXiv 1705.00348 (2017)

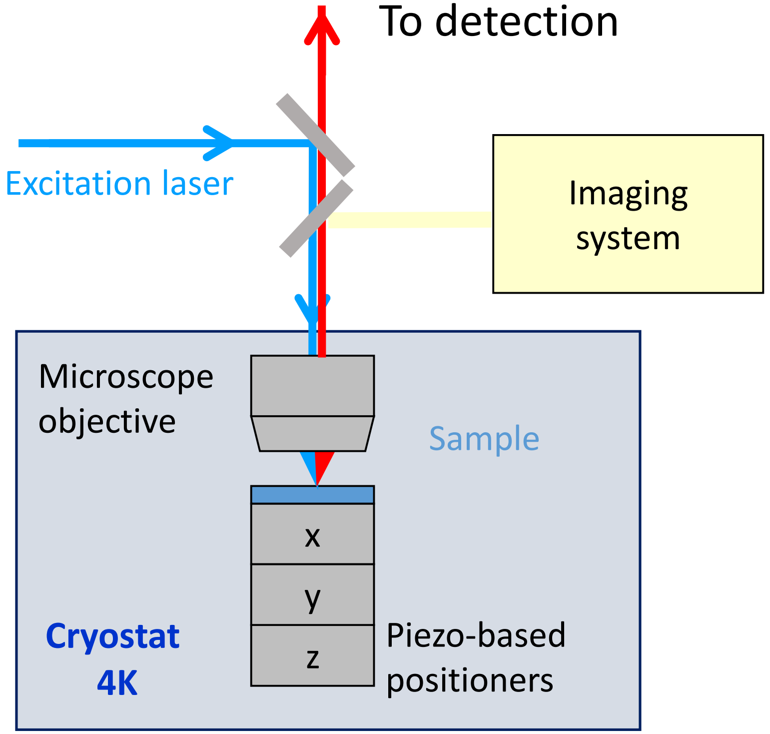
µ-Photoluminescence

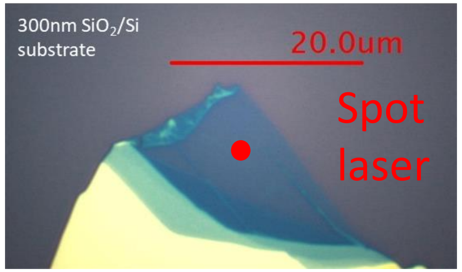
Experimental setup

- Size of monolayer ~10 µm
  → Need for laser spot ~1 µm
  → Precise sample positioning
- Low temperature required
  → Optical cryostat with no vibration & ajustable temperature 4 K – 300 K
- Wavelength-tunable LASER
- Sensitive detector

4K Cryostat



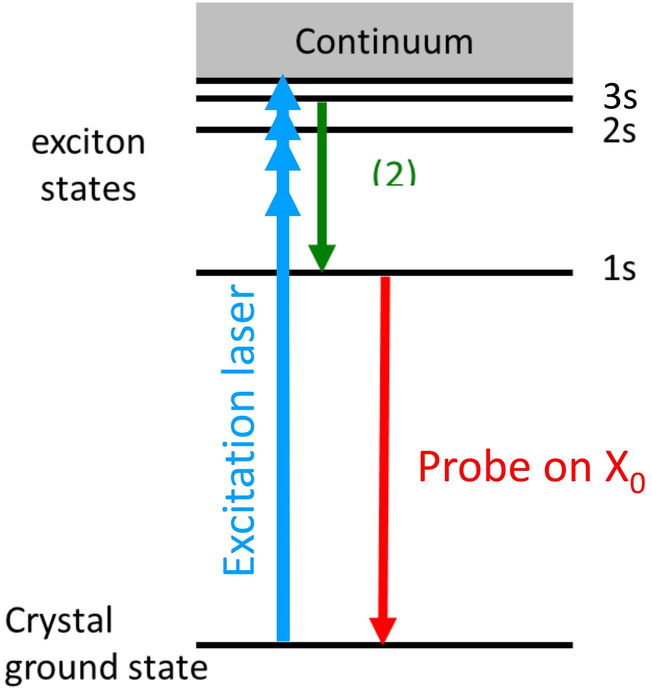


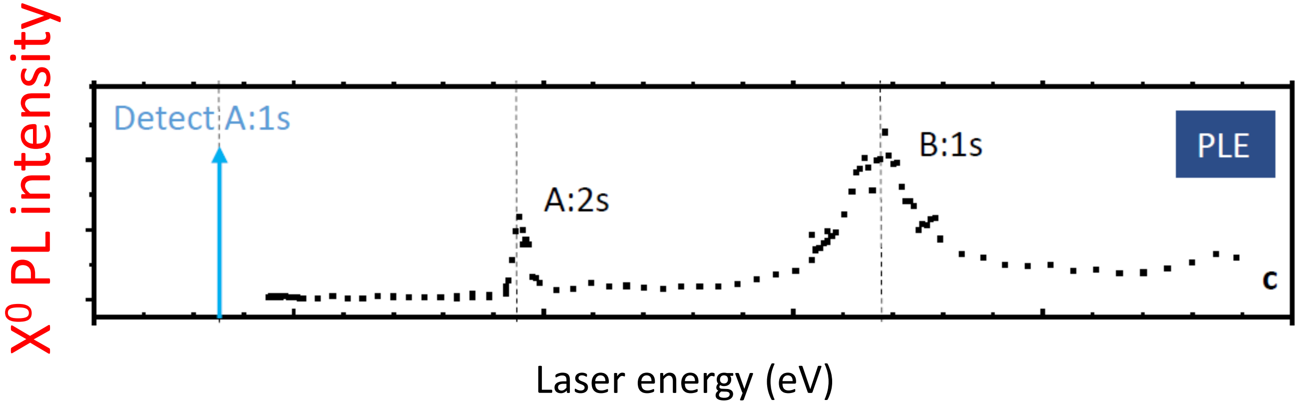


Photoluminescence excitation (PLE)

Ex: TMDC

tuning knob=laser energy





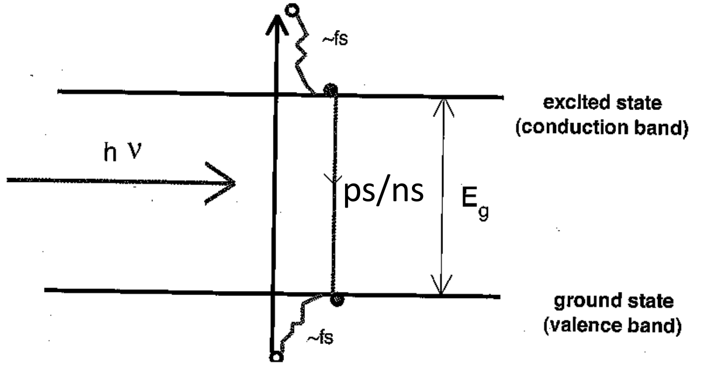
Phys. Rev. Lett. 114, 97403 (2015)

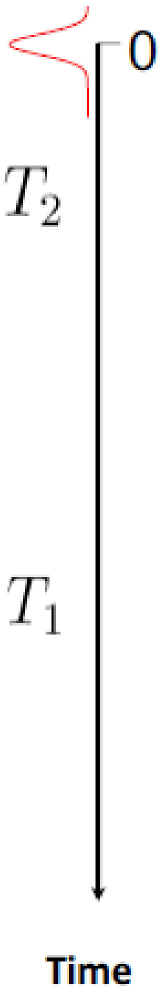
*Probes the density of states but !! Sensitive to relaxation mechanisms
→ different from absorption measurements

*Need for wavelength tunable laser source

Time-resolved spectroscopy

tuning knob=time





- **Coherent Regime (< 1 ps)**

- momentum scattering
- carrier-carrier scattering
- carrier-optical phonons

Four-Wave Mixing

- **Non-Thermal Regime (few ps)**

  - e-h scattering
  - intersubband scattering
  - capture

- **Hot-Thermal Regime (< 100 ps)**

  - phonon scattering (acoustic, optical)

- **Equilibrium with lattice (ns)**

- recombination (radiative and non-radiative)

- Pump-probe
- TR-Photolum.

Time-resolved PL

*Information on the dynamics of the carrier population
*Information on relaxation times
*Information on radiative or non-radiative recombination channels

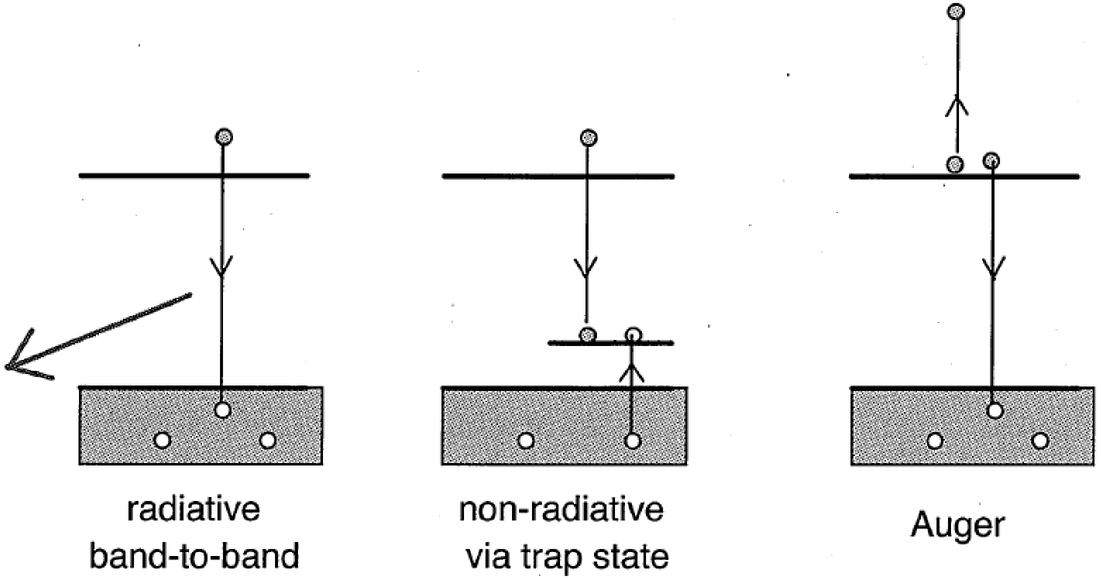
$$\boxed{\frac{dn}{dt} = -An - Bn^2 - Cn^3}$$

Hypothesis: n=p

A: recombination coefficient on defects $A \sim \frac{1}{\tau_{non-rad}}$

B: radiative recombination coefficient $B \sim \frac{1}{\tau_{rad}}$

C: non-radiative recombination coefficient, type Auger



Time-resolved PL

☐ With fast-detection electronics (ns and slower)

☐ With intensified CCD (ICCD) cameras (>=500 ps)

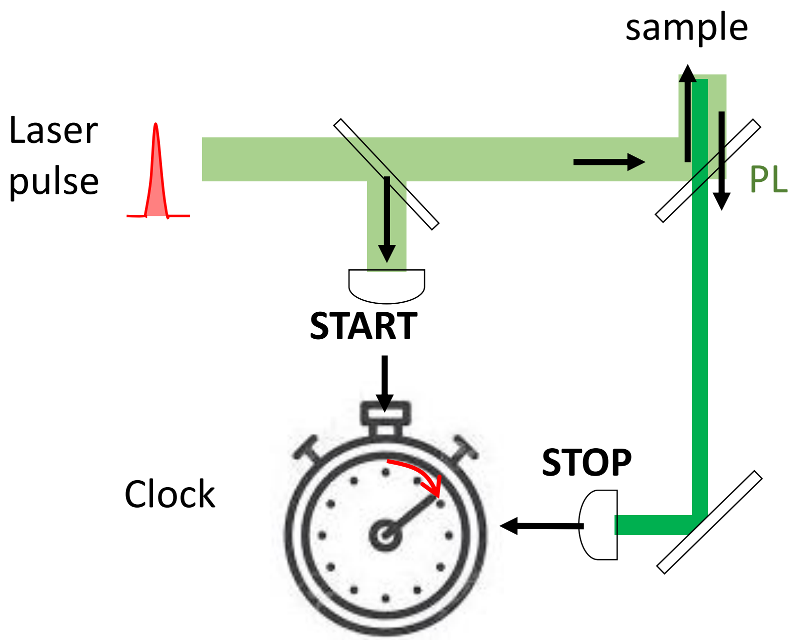
☐ With Avalanche Photodiode (SPAD, APD)
or Time Correlated Single Photon Counting TCSPC (ps and slower)

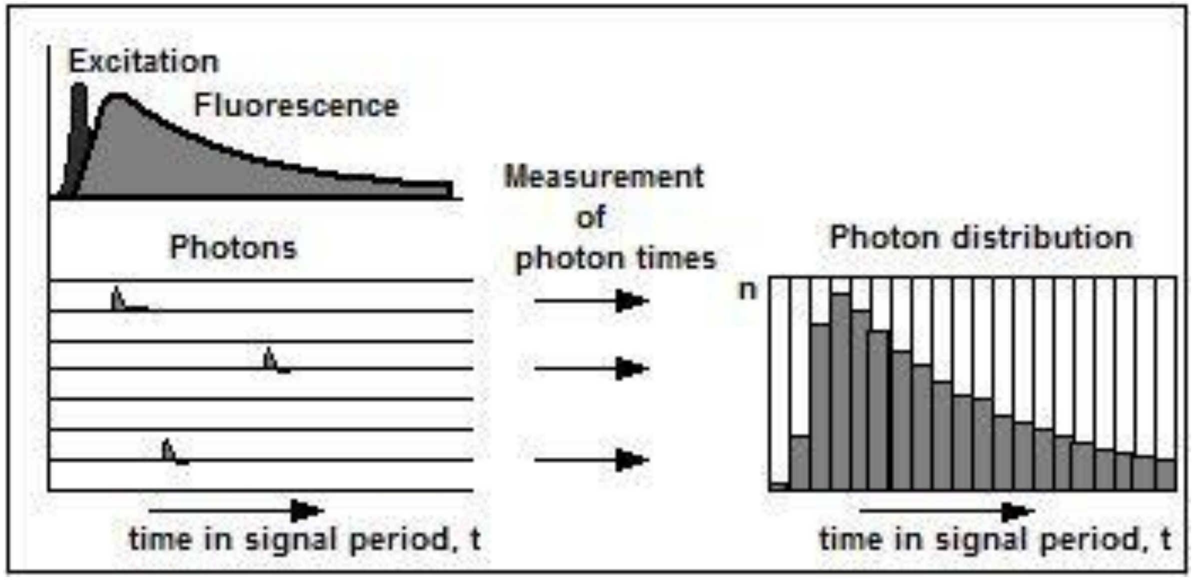
☐ With a Streak camera (<ps and slower)

☐ With optical gating (fs and slower)

Time-resolved PL

With time-correlated single photon counting system (TCSPC)





Photons can be detected by photodetectors with intrinsically high gain such as photomultipliers / micro-channel plate / single photon avalanche photodiodes (SPAD)

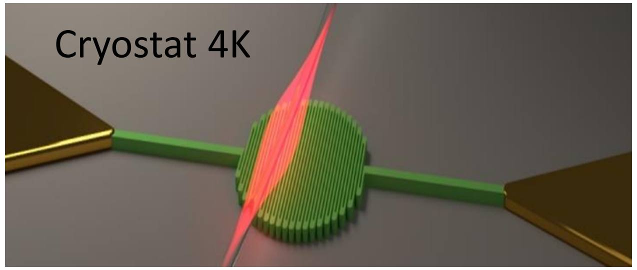
TCSPC can be used to measure lifetimes ranging from <50 ps to over 50 ms

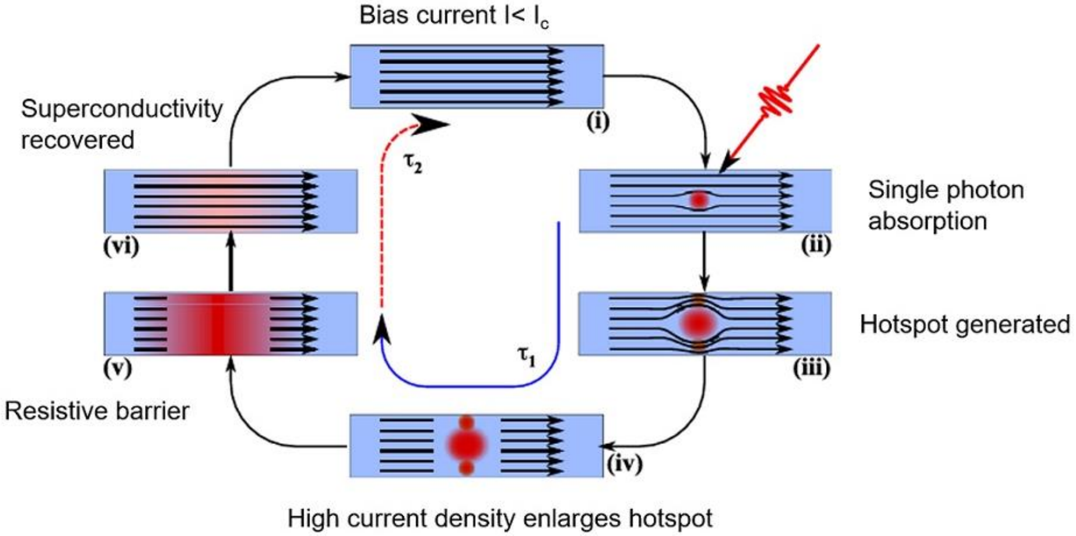
+ Cheap

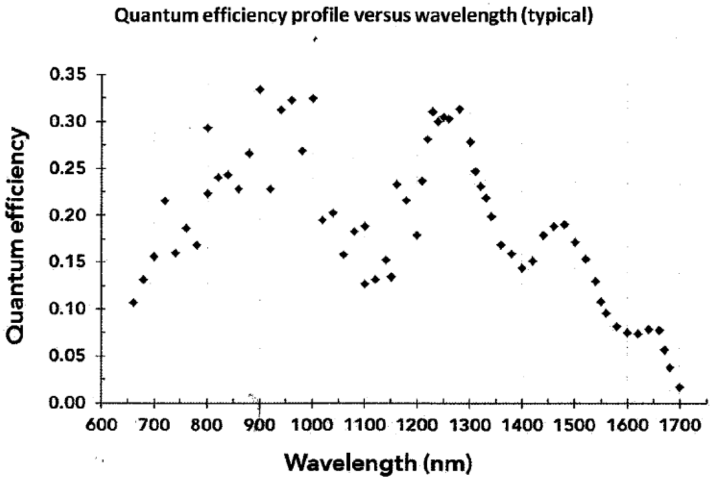
− single-channel
single photon : to be repeated a large number of times to get good S/N signal

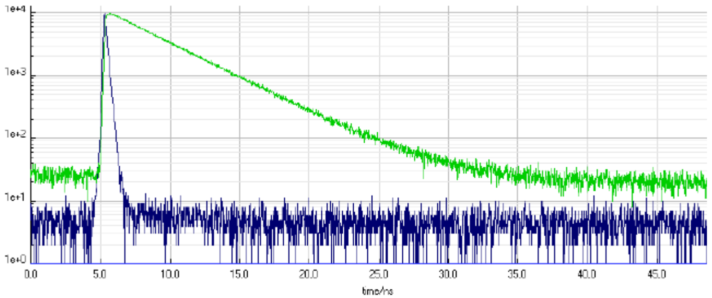
Time-resolved PL

With superconducting nanowire single photon detector (SNSPD)







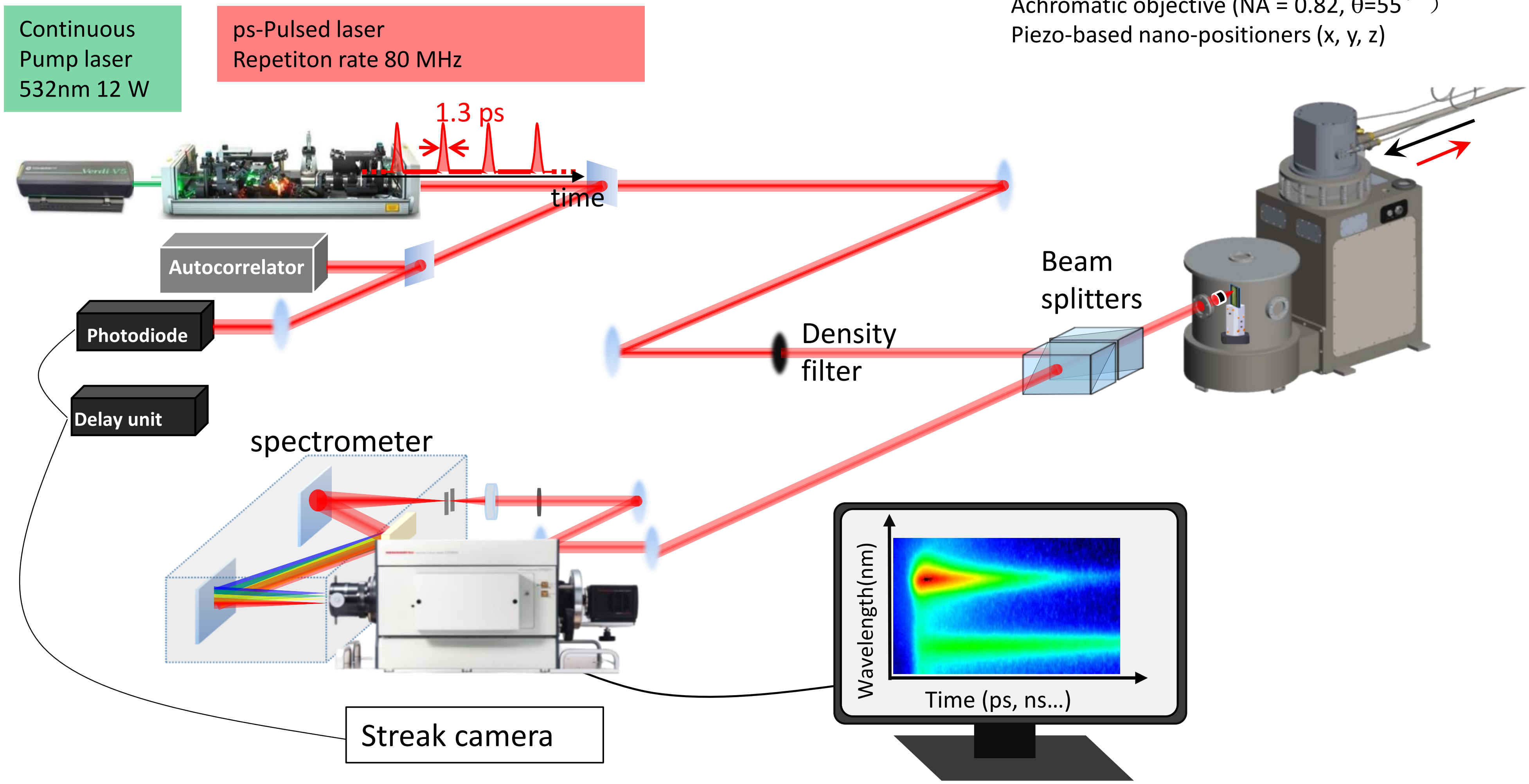


- Can detect single photons with high efficiency over a broad spectral range (even NIR)
- High timing resolution of less than 50 ps

Time-resolved PL

With streak camera

Closed-cycle Cryostat: 4K to RT
Achromatic objective (NA = 0.82, θ=55°)
Piezo-based nano-positioners (x, y, z)



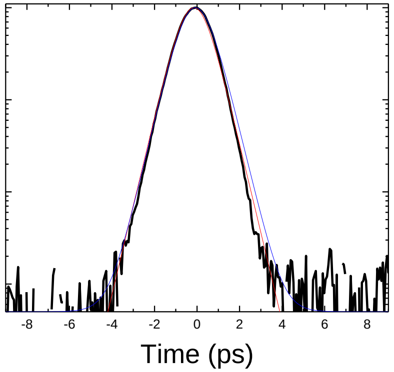
PL intensity as a function of wavelength and time

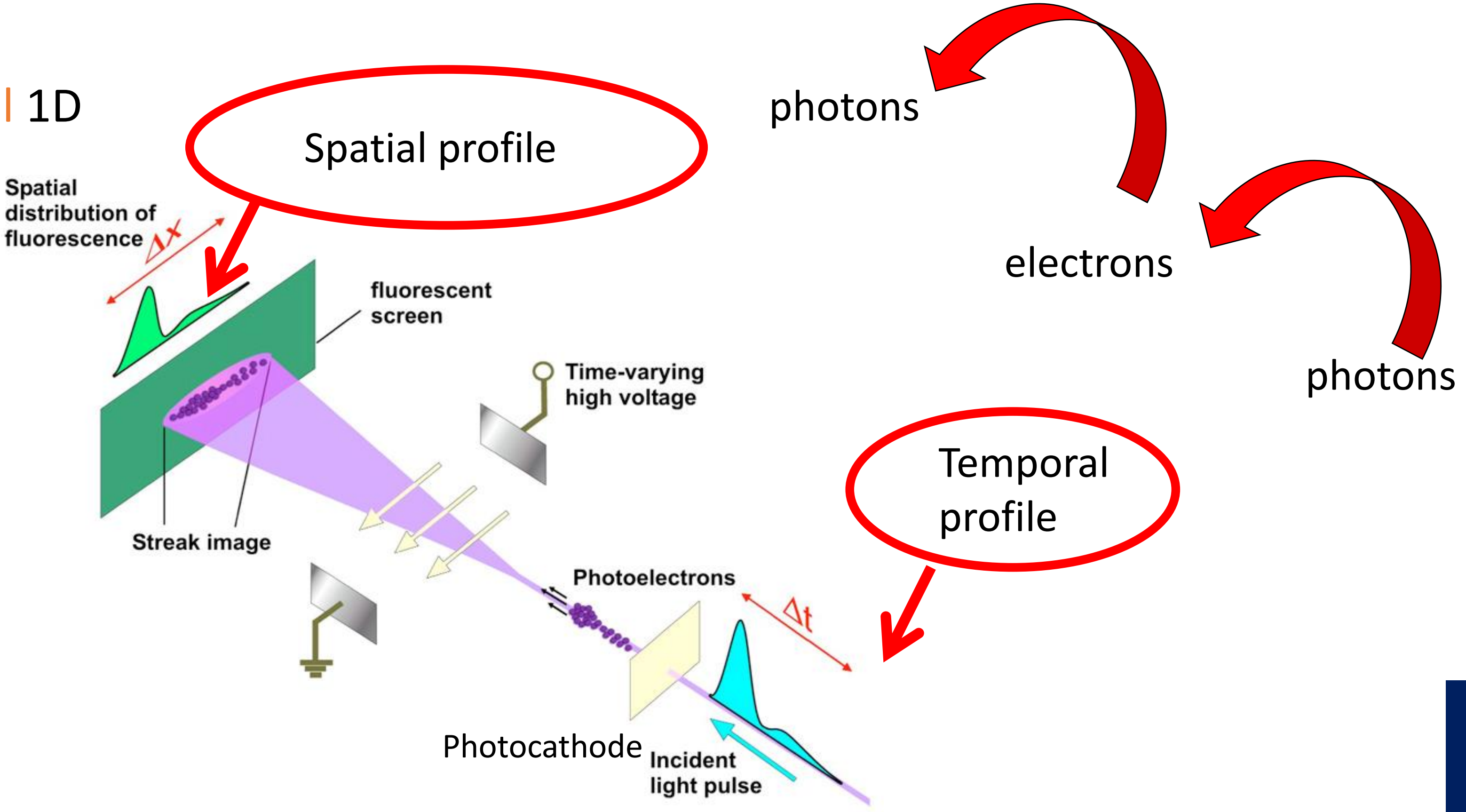
Time-resolved PL

With streak camera

- ✓ Time resolution (few ps)
  - Rep rate up to 80MHz
- ✓ Spectral resolution or spatial 1D
- ✓ Luminescence flux
- ✓ Time resolution <1 ps

Instrument response function (IRF)

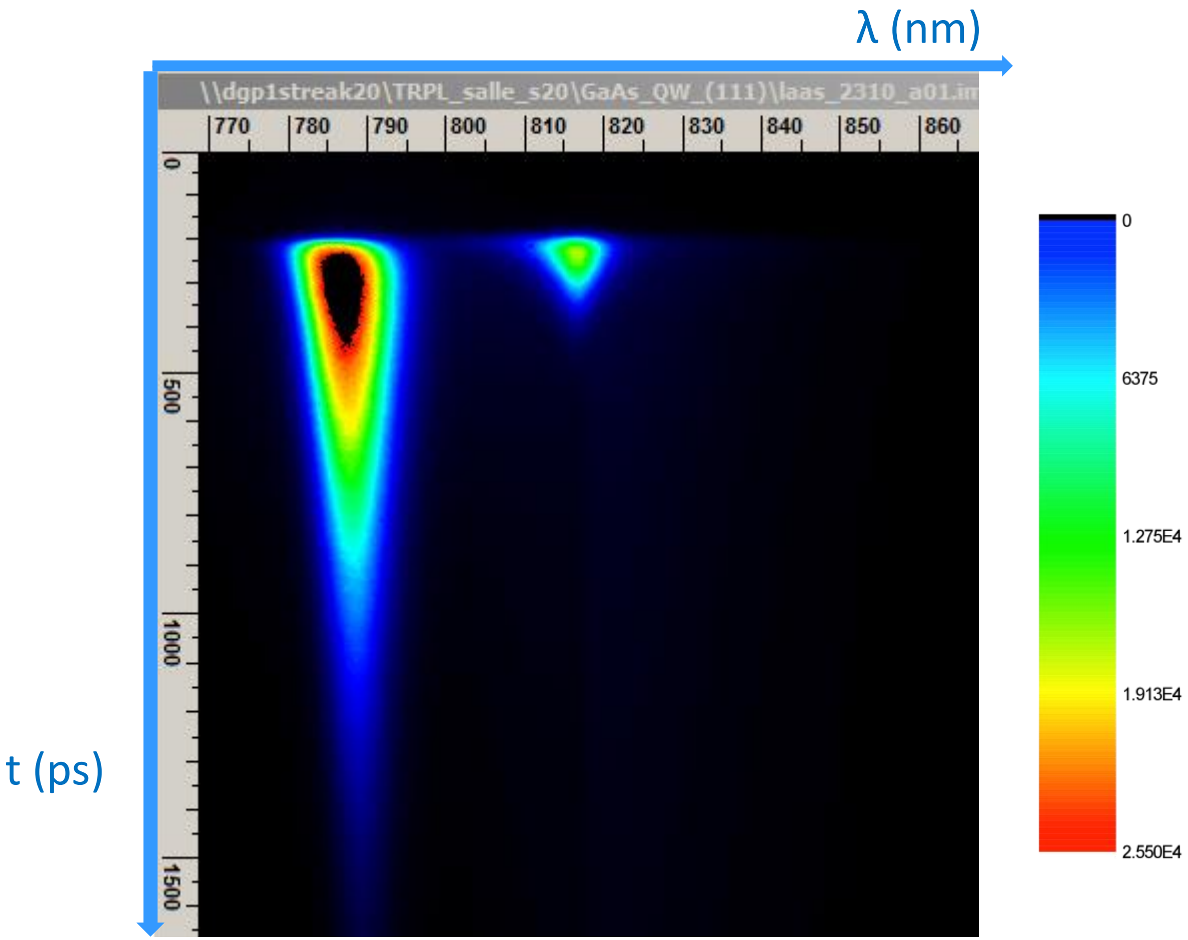




Time-resolved PL

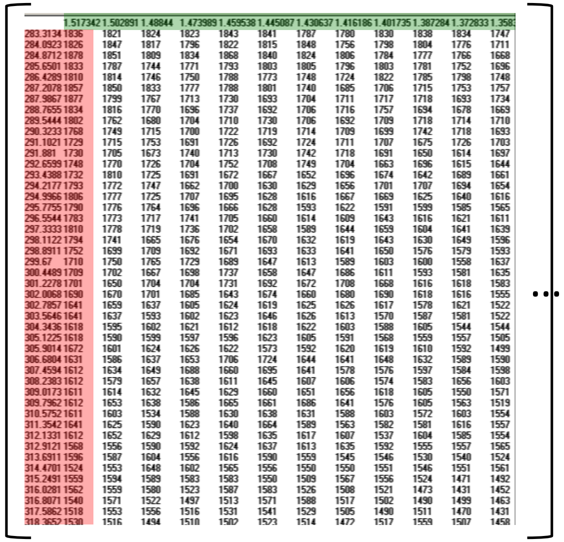
With streak camera

« **tridimensionnal** » images = time + intensity + spectrum



Intensity by color coding

M=



	1.517342	1.502891	1.48844	1.473989	1.459538	1.445087	1.430637	1.416186	1.401735	1.387284	1.372833	1.3583
283.3134	1836	1821	1824	1823	1843	1841	1787	1780	1830	1838	1834	1747
284.0923	1826	1847	1817	1796	1822	1815	1848	1756	1798	1804	1776	1711
284.8712	1878	1851	1809	1834	1868	1840	1824	1806	1784	1777	1766	1668
285.6501	1833	1787	1744	1771	1793	1803	1805	1796	1803	1781	1752	1696
286.4289	1810	1814	1746	1750	1788	1773	1748	1724	1822	1785	1798	1748
287.2078	1857	1850	1833	1777	1788	1801	1740	1685	1706	1715	1753	1757
287.9867	1877	1799	1767	1713	1730	1693	1704	1711	1717	1718	1693	1734
288.7655	1834	1816	1770	1696	1737	1692	1706	1716	1757	1694	1678	1669
289.5444	1802	1762	1680	1704	1710	1730	1706	1692	1709	1718	1714	1710
290.3233	1768	1749	1715	1700	1722	1719	1714	1709	1699	1742	1718	1693
291.1021	1729	1715	1753	1691	1726	1692	1724	1711	1707	1675	1726	1703
291.881	1730	1705	1673	1740	1713	1730	1742	1718	1691	1650	1614	1697
292.6599	1748	1770	1726	1704	1752	1708	1749	1704	1663	1696	1615	1644
293.4388	1732	1810	1725	1691	1672	1667	1652	1696	1674	1642	1689	1661
294.2177	1793	1772	1747	1662	1700	1630	1629	1656	1701	1707	1694	1654
294.9966	1806	1777	1725	1707	1695	1628	1616	1667	1669	1625	1640	1616
295.7755	1790	1776	1764	1696	1666	1628	1593	1622	1591	1599	1585	1565
296.5544	1783	1773	1717	1741	1705	1660	1614	1609	1643	1616	1621	1611
297.3333	1810	1778	1719	1736	1702	1658	1589	1644	1659	1604	1641	1639
298.1122	1794	1741	1665	1676	1654	1670	1632	1619	1643	1630	1649	1596
298.8911	1752	1699	1709	1692	1671	1693	1633	1641	1650	1576	1579	1593
299.67	1710	1750	1765	1729	1689	1647	1613	1589	1603	1600	1558	1637
300.4489	1709	1702	1667	1698	1737	1658	1647	1686	1611	1593	1581	1635
301.2278	1701	1650	1704	1704	1731	1692	1672	1708	1668	1616	1618	1583
302.0068	1690	1670	1701	1685	1643	1674	1660	1680	1690	1618	1616	1555
302.7857	1641	1659	1637	1605	1624	1619	1625	1626	1617	1578	1621	1522
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305.1225	1618	1590	1599	1597	1596	1623	1605	1591	1568	1559	1557	1505
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308.2383	1612	1579	1657	1638	1611	1645	1607	1606	1574	1583	1656	1603
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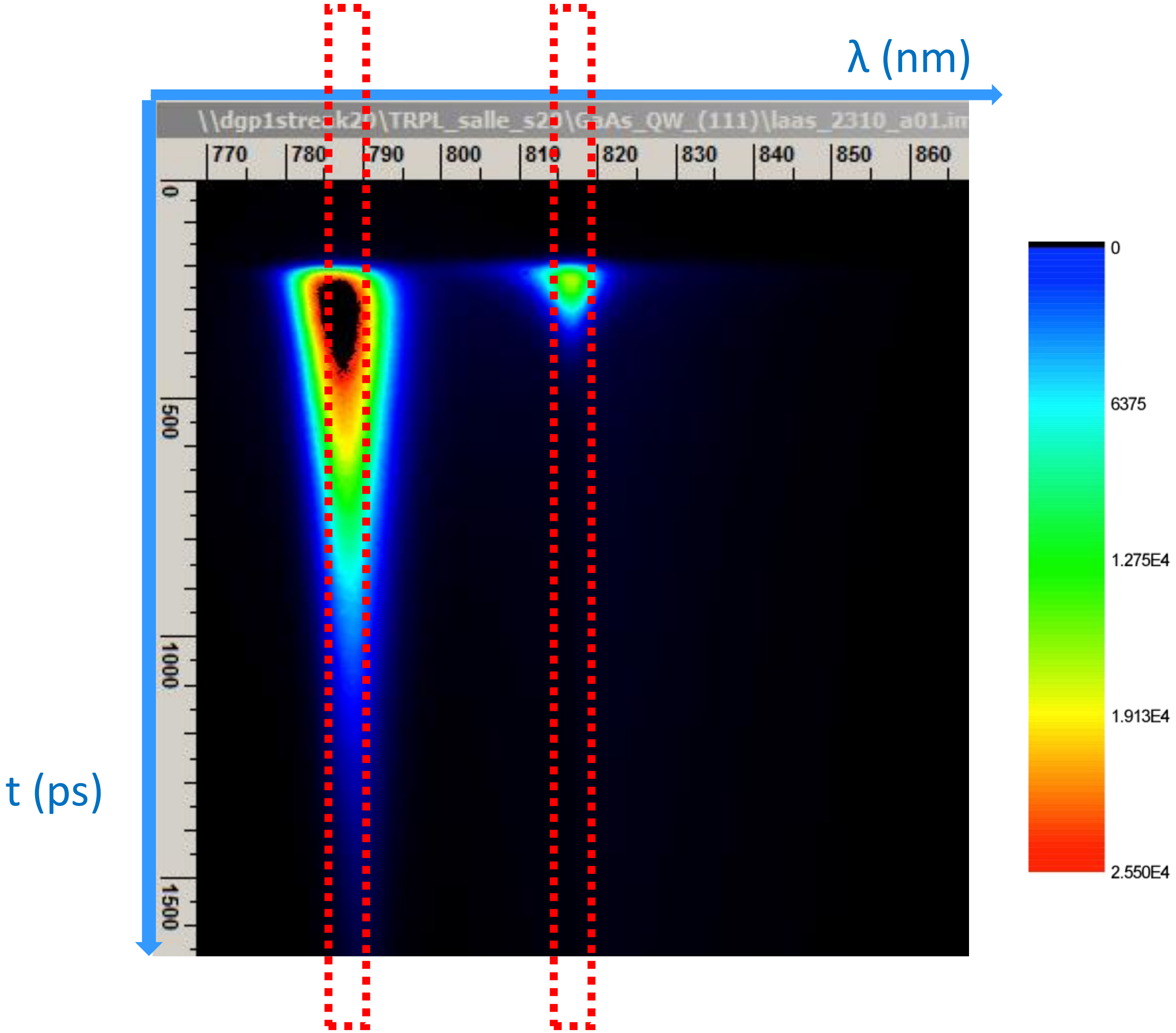
309.7962	1612	1653	1638	1586	1665	1661	1686	1641	1576	1605	1563	1519
310.5752	1611	1603	1534	1588	1630	1638	1631	1588	1603	1572	1603	1554
311.3542	1641	1625	1590	1623	1640	1664	1589	1563	1582	1581	1616	1557
312.1331	1612	1652	1629	1612	1598	1635	1617	1607	1537	1604	1585	1554
312.9121	1568	1556	1590	1592	1624	1637	1613	1635	1592	1555	1557	1565
313.6911	1596	1587	1604	1556	1616	1590	1559	1545	1546	1530	1540	1524
314.4701	1524	1553	1648	1602	1565	1556	1550	1550	1551	1546	1551	1561
315.2491	1559	1594	1589	1583	1583	1550	1509	1567	1556	1524	1471	1492
316.0281	1562	1559	1580	1523	1587	1583	1526	1508	1521	1473	1431	1452
316.8071	1540	1571	1522	1497	1513	1571	1588	1517	1502	1490	1499	1463
317.5862	1518	1553	1556	1516	1531	1541	1529	1505	1490	1511	1470	1431
318.3652	1530	1516	1494	1510	1502	1523	1514	1472	1517	1559	1507	1458

…

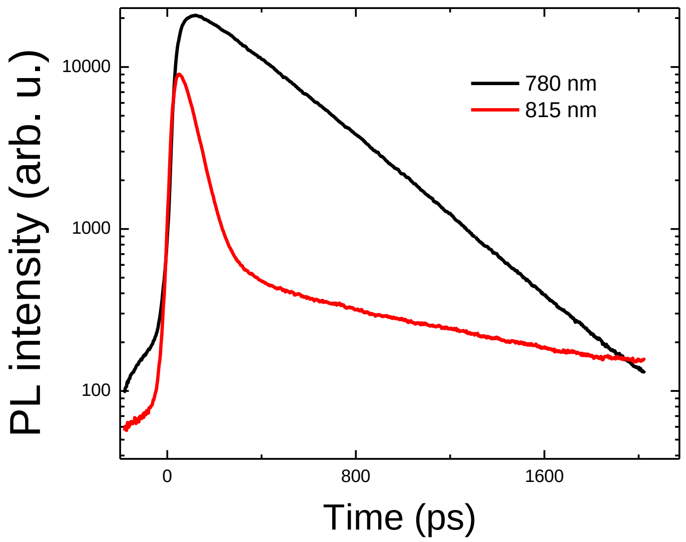
Time-resolved PL

With streak camera

« **tridimensionnal** » images = time + intensity + spectrum



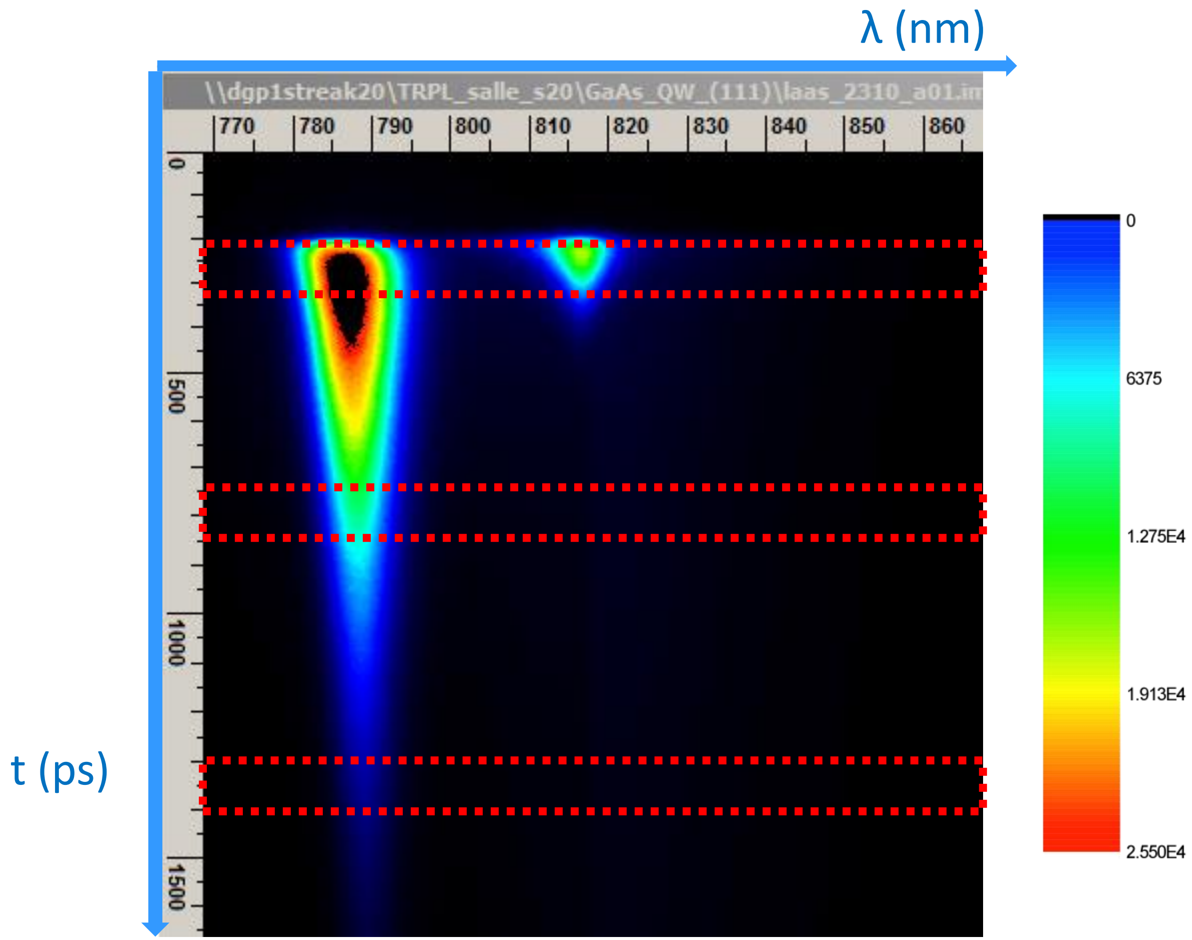
Spectral selection



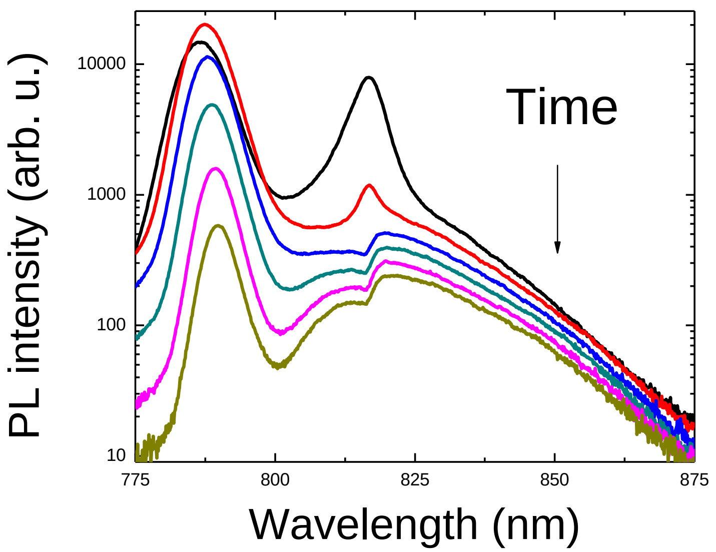
Time-resolved PL

With streak camera

« **tridimensionnal** » images = time + intensity + spectrum



« Slices » of time delay

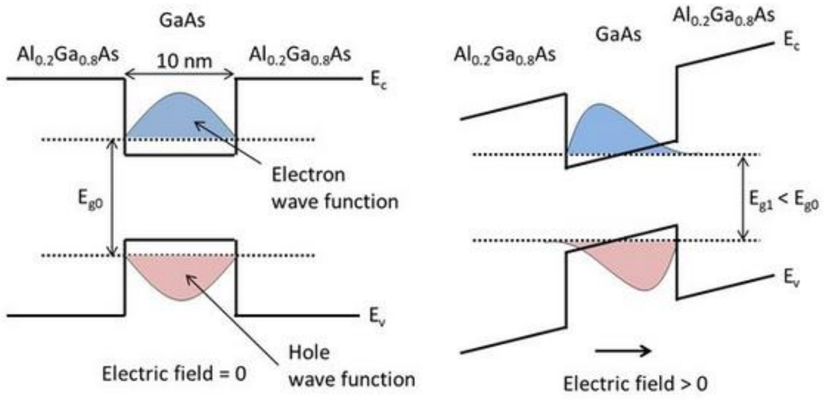


- Carrier cooling
- Diffusion
- …

Time-resolved PL

Ex: Quantum wells

Internal or external electric field on QW:



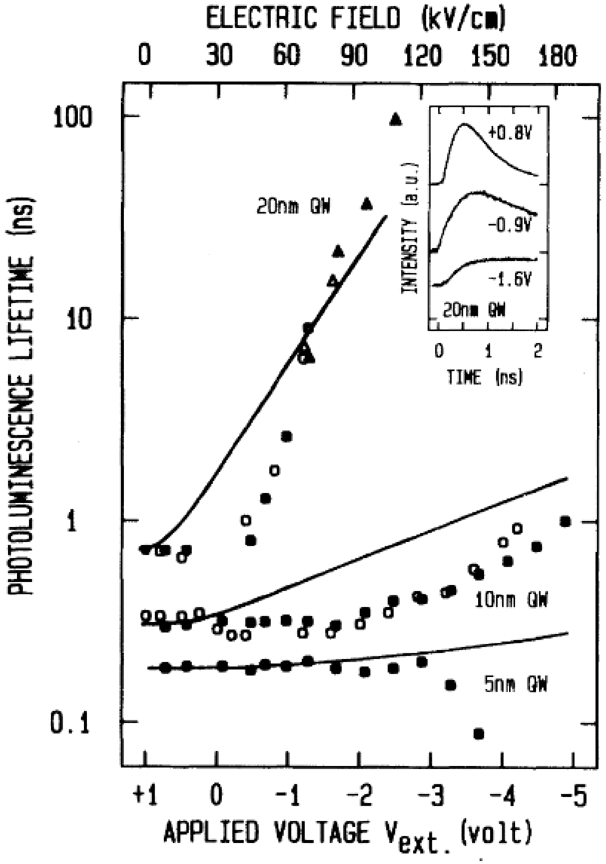
$$B_{vc} = \frac{\pi q^2}{2\hbar} \cdot \left|\langle \Psi_c(r) | E.\hat{r} | \Psi_v(r) \rangle\right|^2 \times \delta(E_c - E_v - \hbar\omega)$$

Einstein coefficient

Coupling of Ψ_V to Ψ_C

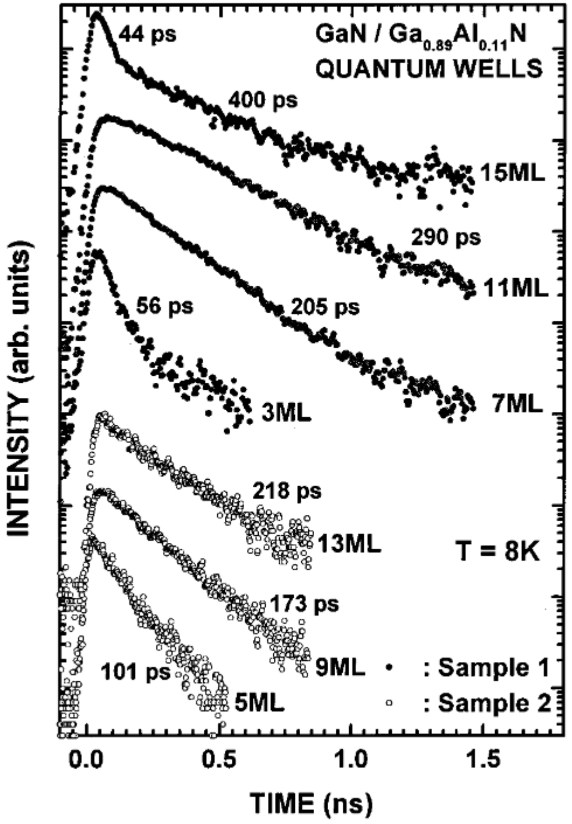
*Plays with the electron and hole wavefunction overlap
*Increase of QW decay times with E

GaAs QW



Phys. Rev. Lett. 55, 2610 (1985)

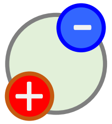
GaN QW



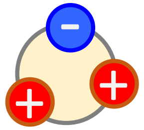
Phys. Rev. B 59, 15363 (1999)

Time-resolved PL

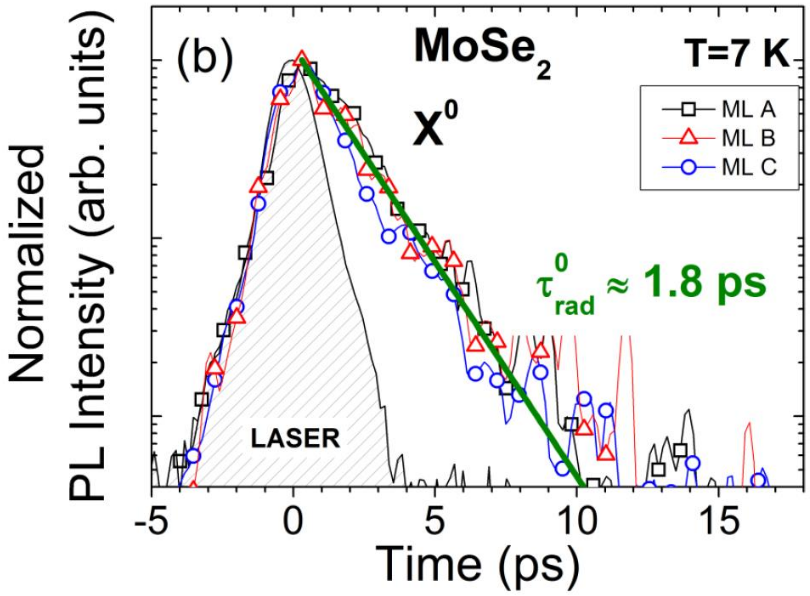
Ex: TMDC

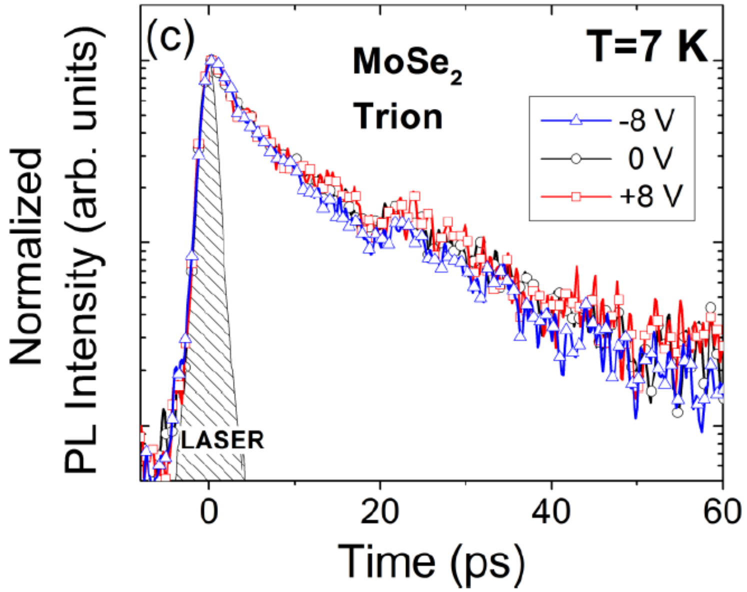


Neutral exciton



Charged exciton
(negative or positive) = trions





Exciton radiative lifetime ~1.8 ps

Exciton Bohr radius ~0.5 nm

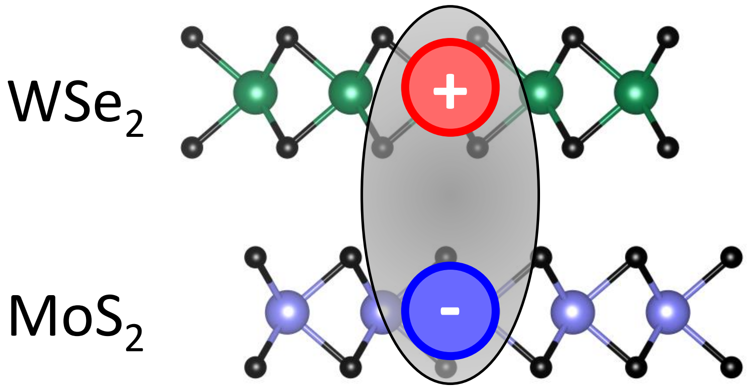
Trion decay ~15 ps

PRB **93**, 205423 (2016)

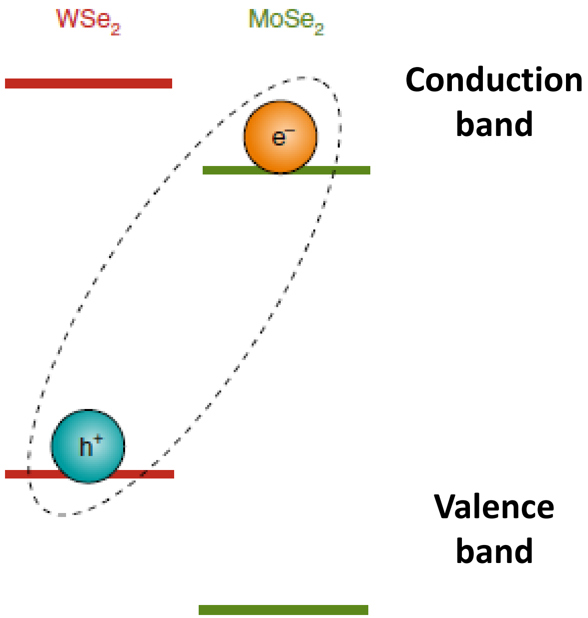
Time-resolved PL

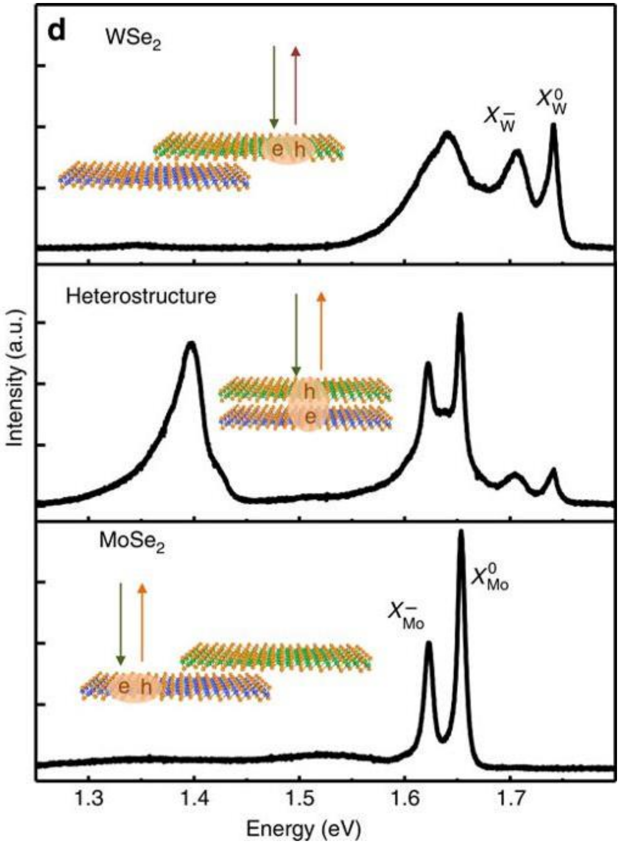
Ex: TMDC heterostructure

Spatially indirect excitons



Type II band alignment

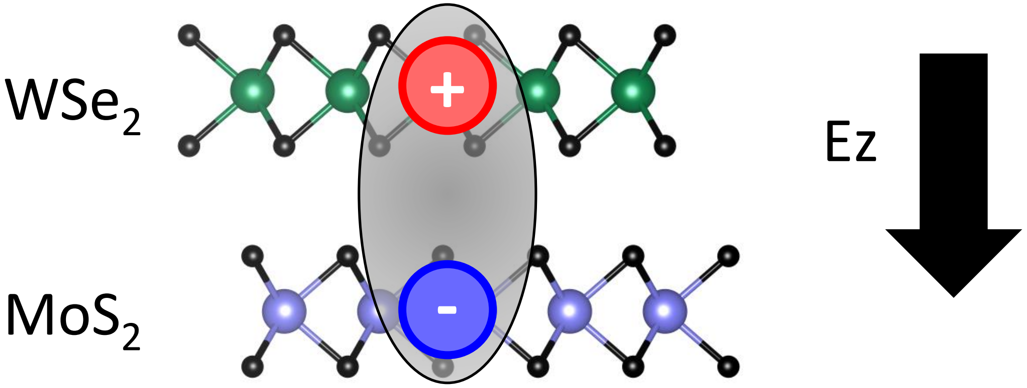




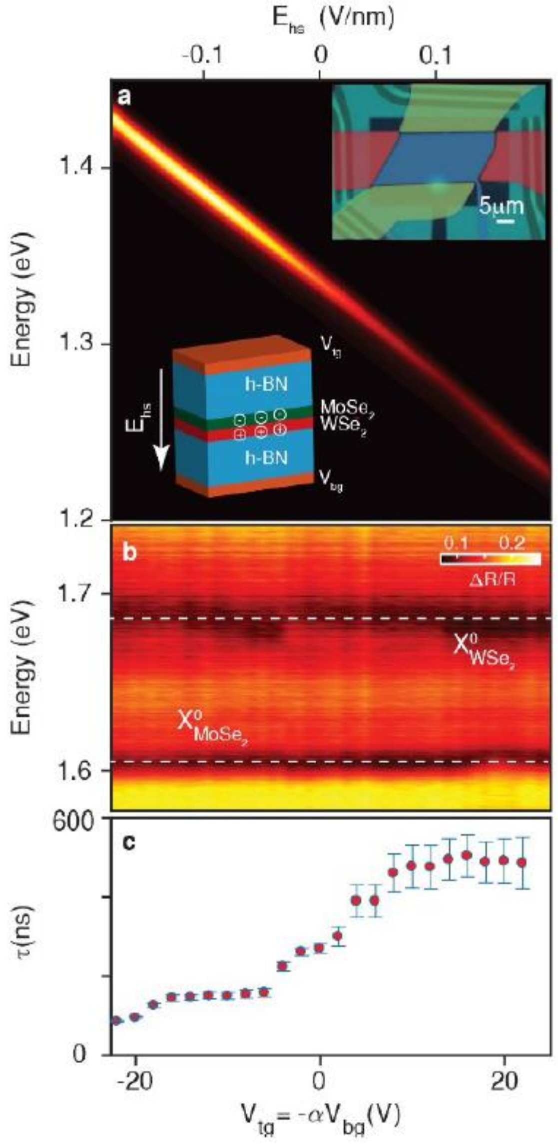
Nat. Comm. **6**, 6242 (2015)

Time-resolved PL

Ex: TMDC heterostructure



Tuning of indirect exciton lifetime with electric field
From ~250ns to 600 ns for E_{hs} > 0.1 V/nm

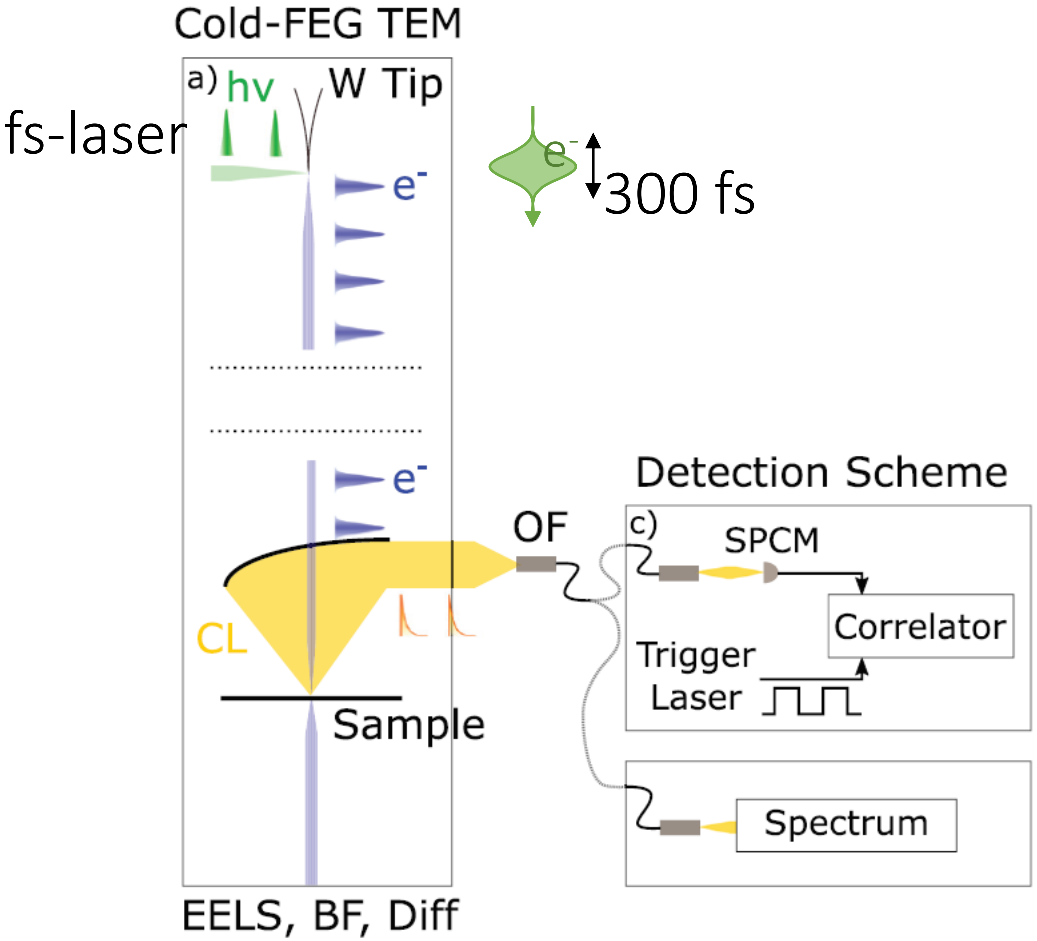


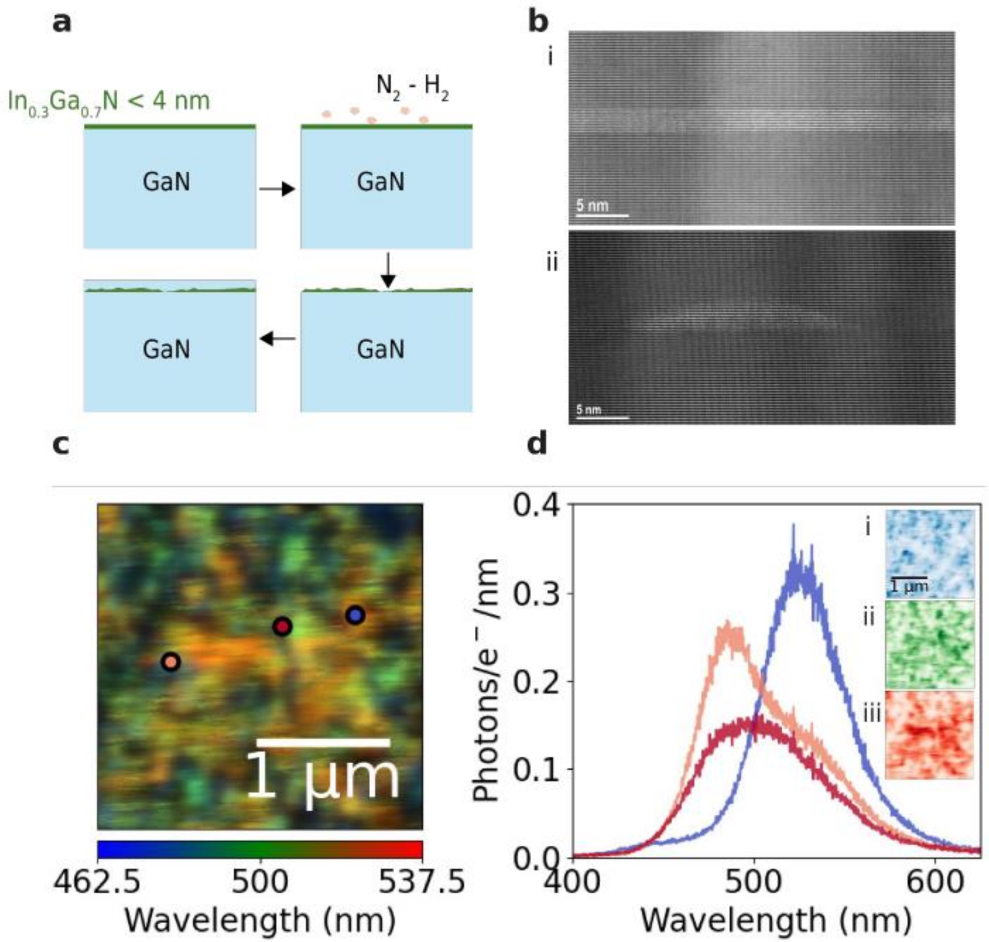
Stark effect

Science 366, 870 (2019)

Time-resolved Cathodoluminescence

Ex: InGaN quantum wells/quantum dots





Ultramicroscopy 186, 128 (2018)
Appl. Phys. Lett. 119, 062106 (2021)

➔ Diffusion of Indium creates QW/QD areas

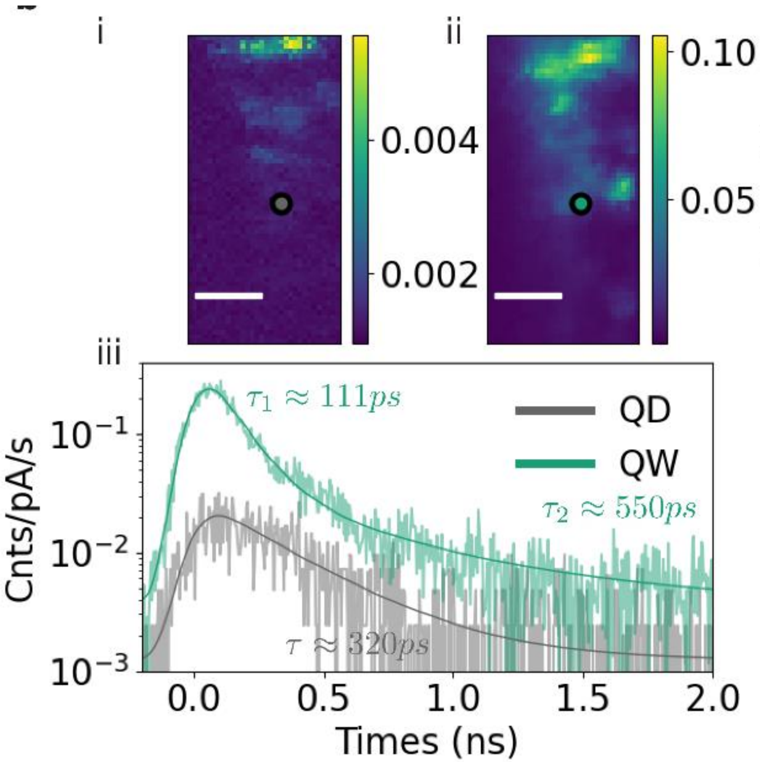
Time-resolved Cathodoluminescence

Ex: InGaN quantum wells/quantum dots

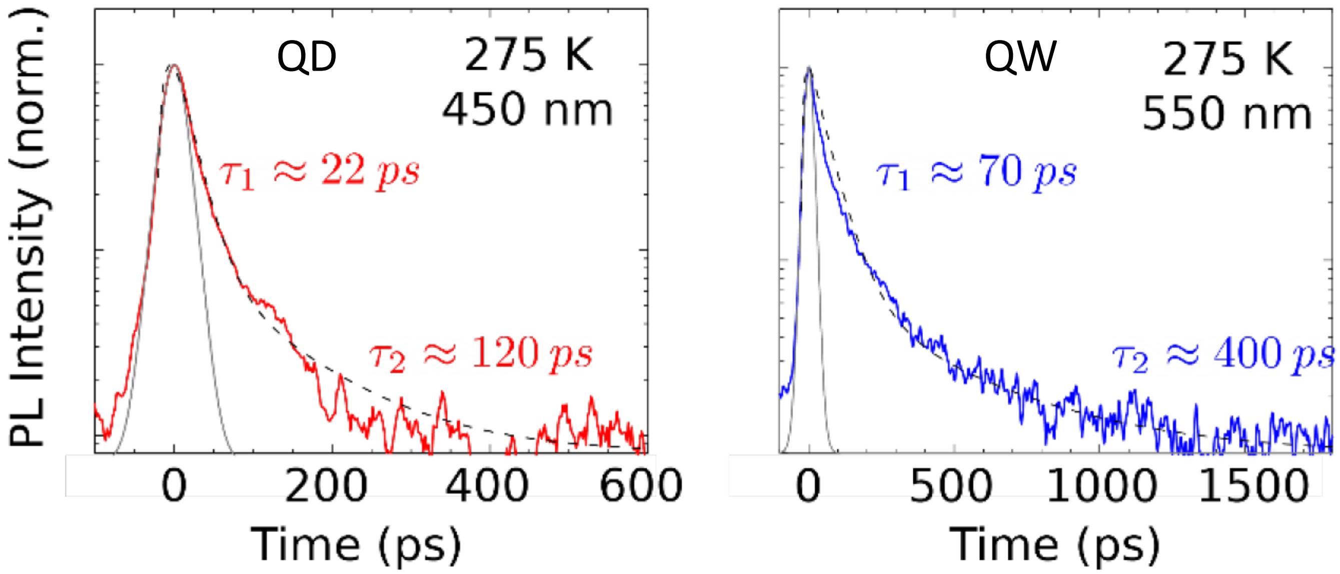
➔ QD ➔ 450 nm and short lifetimes

➔ QW ➔ 550 nm and longer lifetimes

TR-CL



TR-PL



➡ Comparable decays measured by both TR techniques

Outline

Basics of SC physics

* SC band structure
Density of states
Doping

* Interaction with light

* Dimensionality

Optical characterization of SC structures

* Absorption
* Photoemission

* Reflectivity

* Photoluminescence (PL)
– PL Eexcitation (PLE)

* Time-Resolved PL
– TR-Cathodoluminescence

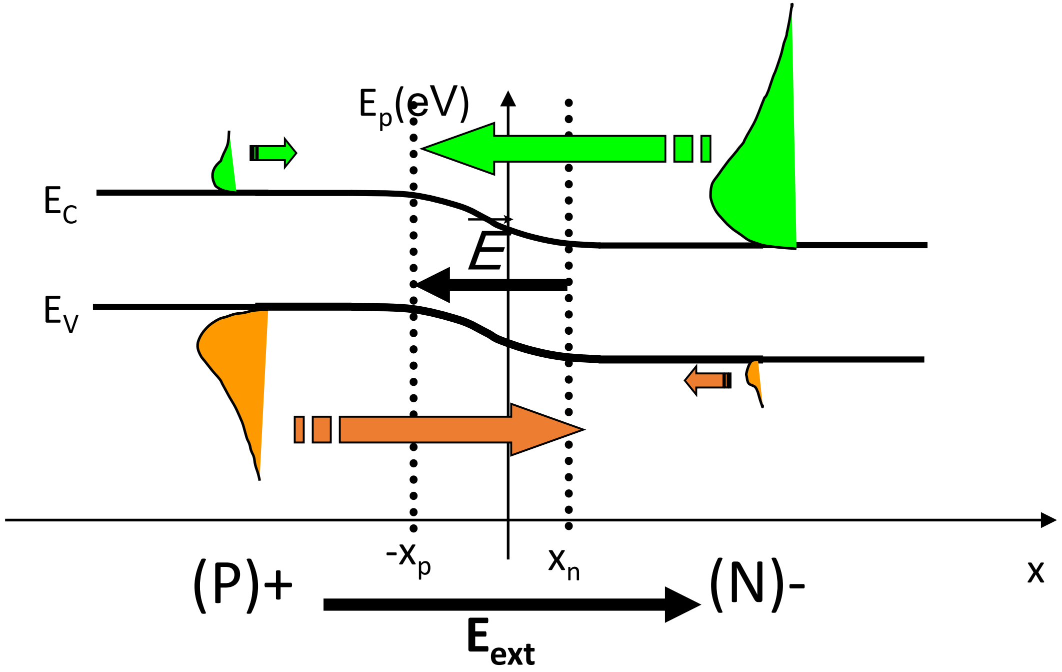
Electric/Optical characterization of SC structures

* Electroluminescence (EL)
* Photocurrent (PC)

Raman spectroscopy

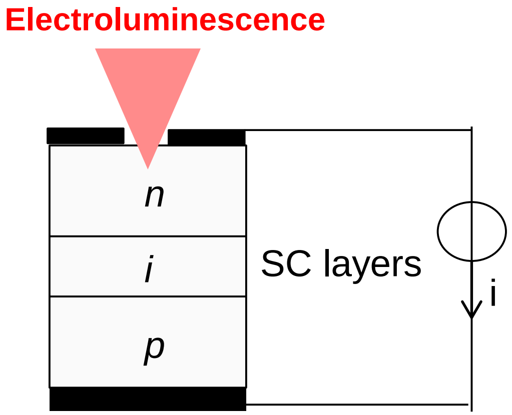
Electro-optical measurements

P(i)N junction

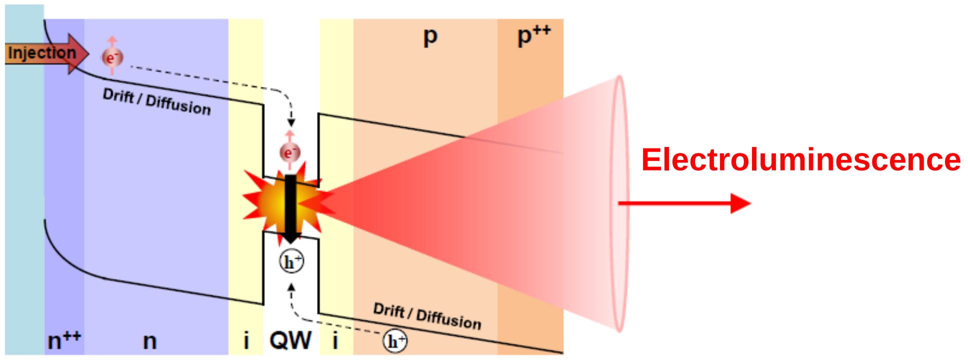


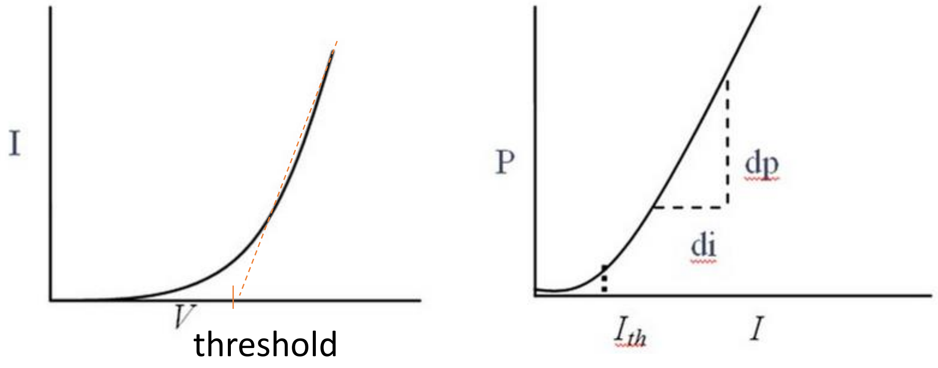
Electroluminescence

*No need for optical excitation
*Need for conductive samples/electric contacts



Sample

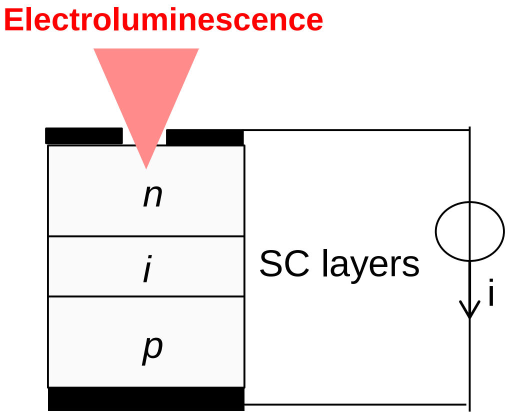




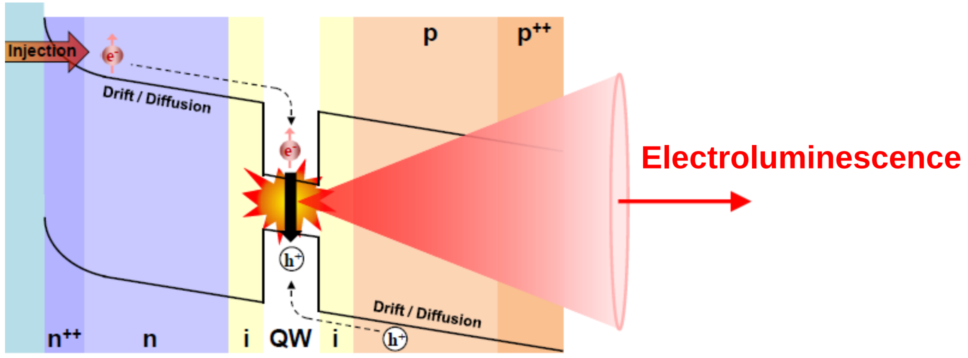
Towards optical devices: LED, laser diode,…

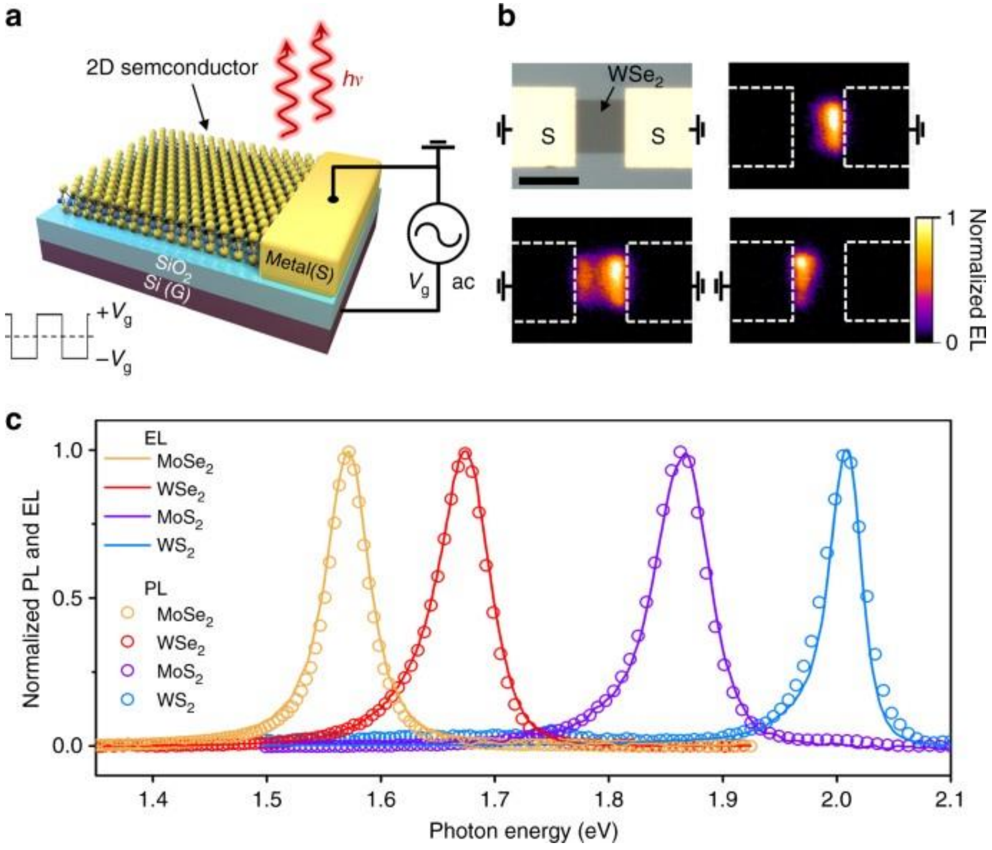
Electroluminescence

*No need for optical excitation
*Need for conductive sample/contacts



Sample

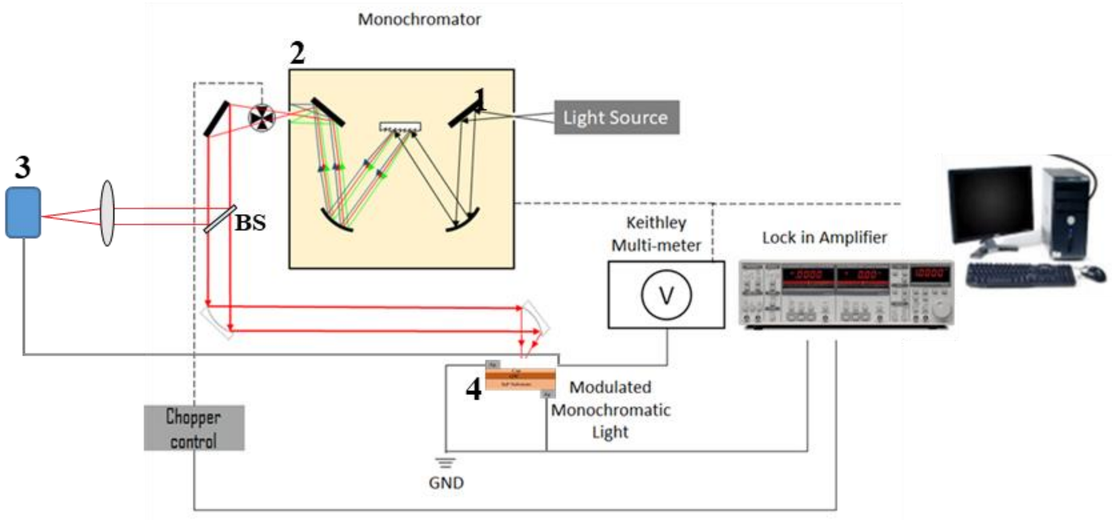




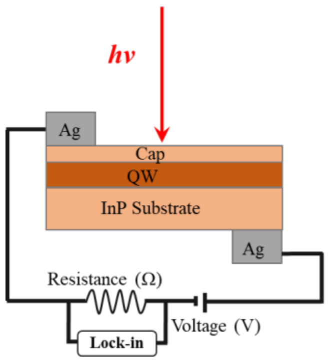
Nature (2016)

Photocurrent spectroscopy

*No need for optical detector
*Need for conductive samples/contacts



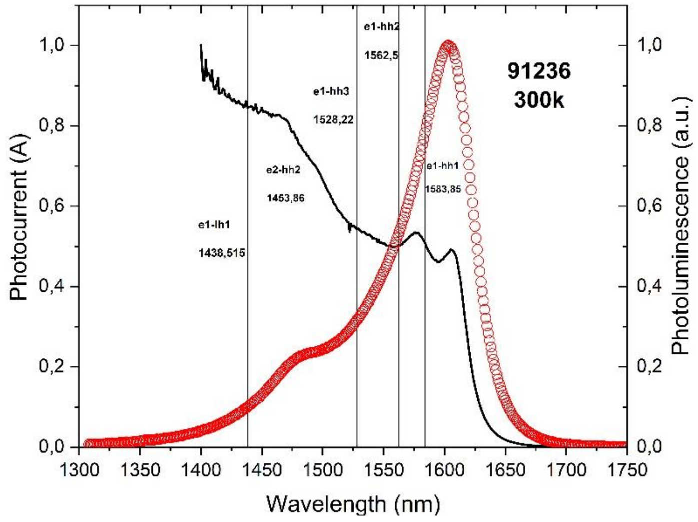
Sample



Ex: Semiconductor Optical Amplifier
based on InGaAsP QWs

Even forbidden transitions
can be observed due to symmetry
breaking by internal electric field

Comparison of PL and PC
with calculated transitions



Outline

Basics of SC physics

* SC band structure
Density of states
Doping

* Interaction with light

* Dimensionality

Optical characterization of SC structures

* Absorption
* Photoemission

* Reflectivity

* Photoluminescence (PL)
– PL Eexcitation (PLE)

* Time-Resolved PL
– TR-Cathodoluminescence

Electric/Optical characterization of SC structures

* Electroluminescence (EL)
* Photocurrent (PC)

Raman spectroscopy

Raman spectroscopy

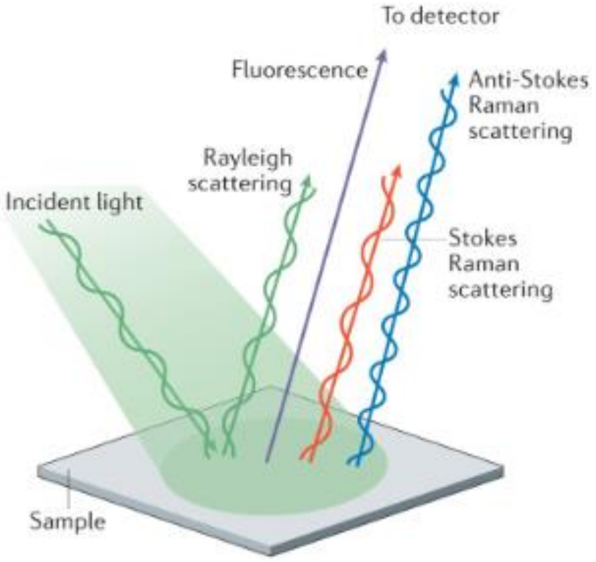
Raman effect:

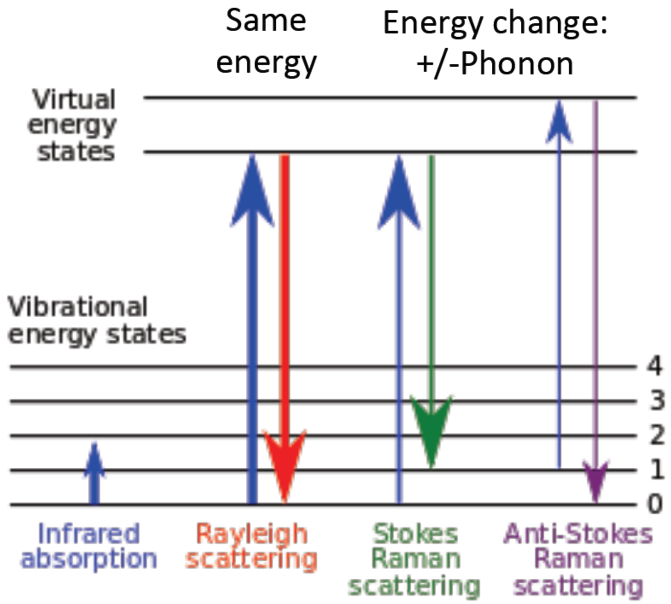
Ineslastic scattering of light under emission or absorption of phonons

Benefits of Raman spectroscopy

Useful in solid state physics, chemistry, biology:

- Crystallographic phase
- Molecule identification
- Chemical bonds analysis
- Characteristic phonon modes
- ...



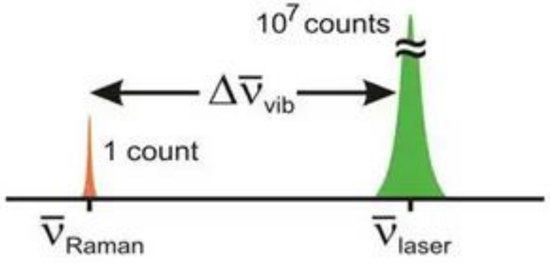


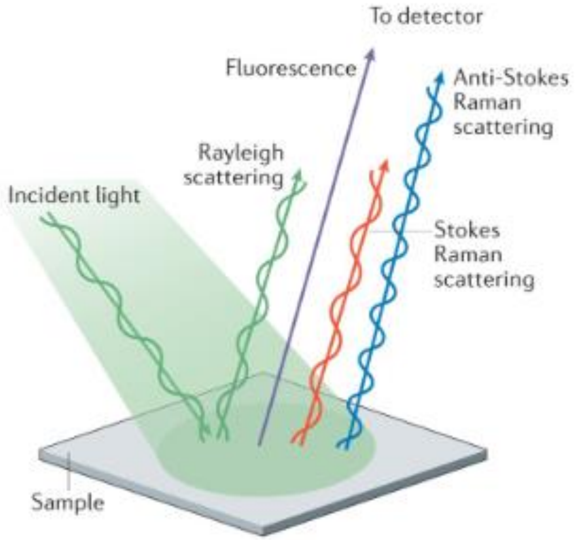
See Anna Fontcuberta i Morral presentation – PULSE Summer school 2015
Introductory Raman spectroscopy 2003

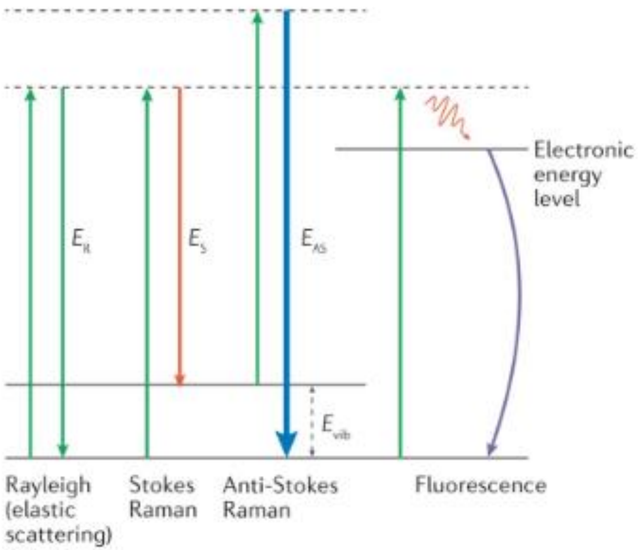
Raman spectroscopy

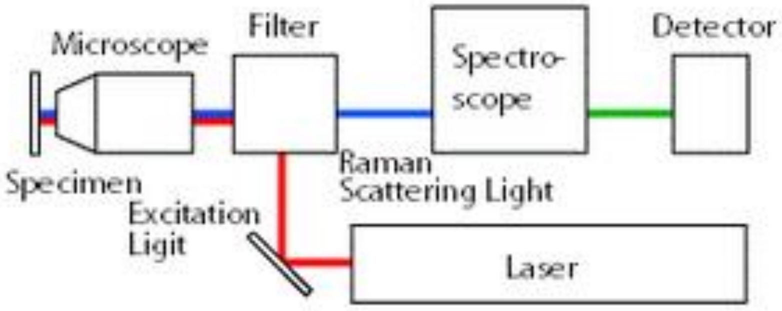
Experimental setup

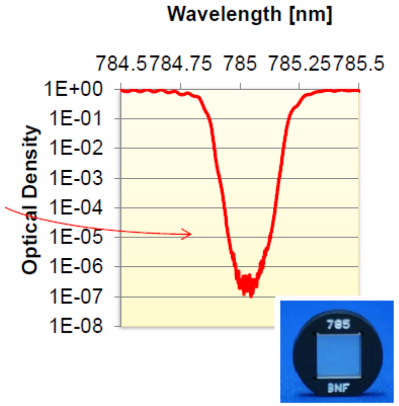
$$\frac{\text{Stokes Raman scattering}}{\text{Rayleigh scattering}} \approx 10^{-7}$$











Difficulties:
*Weak Raman signal
*Raman signal needs to be filtered out of laser light

Unit: cm-1

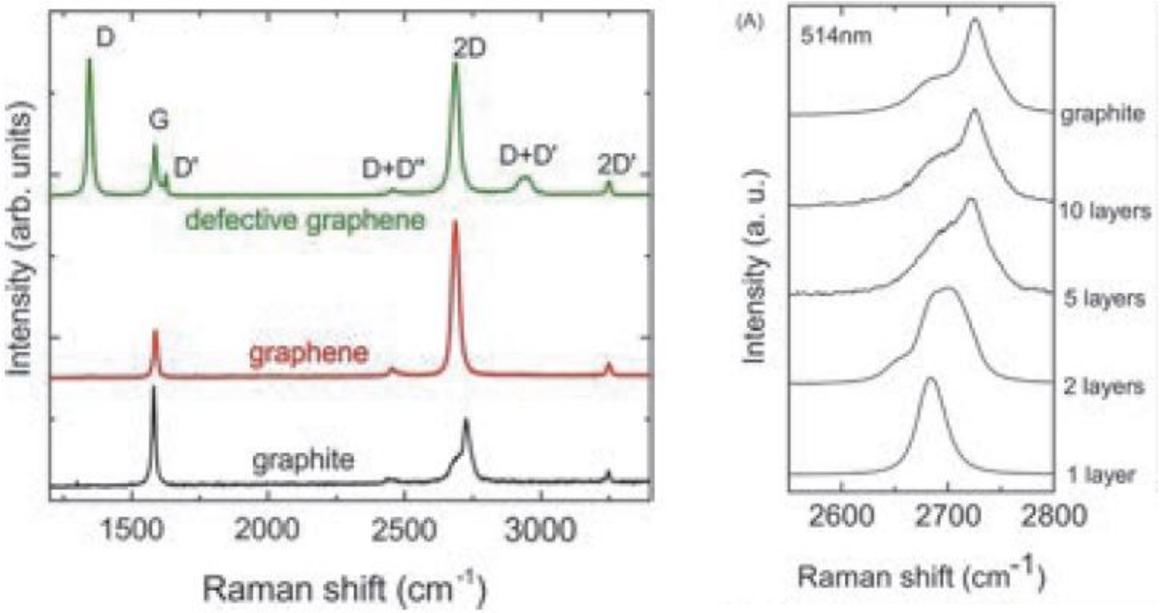
Laser: narrow line (atomic/cavity filtered)

Notch Filter/Spectrometer
with high rejection rates

Raman spectroscopy

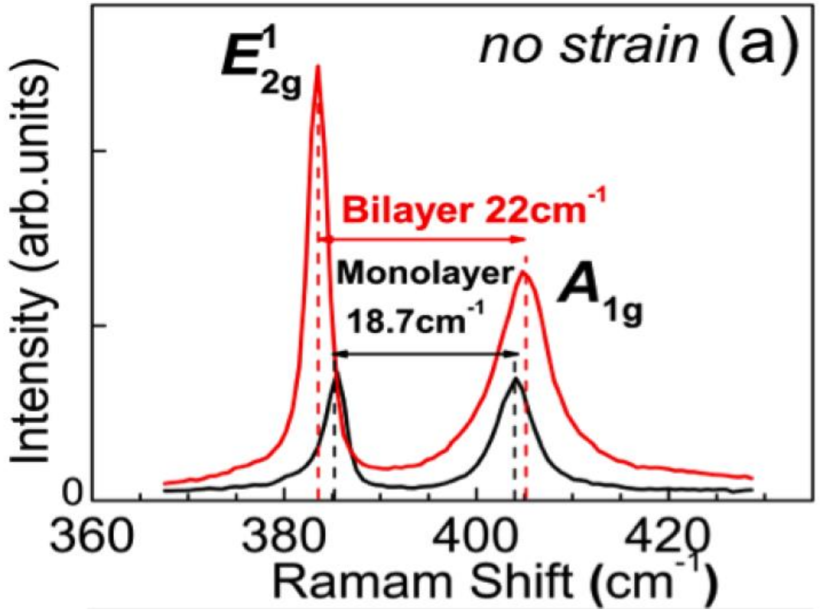
On 2D materials

On graphene



Ferrari et al., Nature Nano 8, 235 (2013)

On TMDC



Appl. Phys. Lett. 99, 102109 (2011)

→ Determination of number of graphene layers

Conclusions

Review of some common techniques from the « optical spectroscopy toolbox »:
Absorption, Reflectivity, Transmission, Photoluminescence

Identify intrinsic and extrinsic optical properties of a SC structure playing with tuning knobs

- Temperature
- Laser energy (=PLE)
- Laser power
- Time (=time-resolved photoluminescence)
- Doping (resident electrons or hole densities)
- Electric field
- Light polarization (excitation and detection)
- Magnetic field (in-plane, out-of-plane)
- Dielectric environment
- Strain
- Direction of propagation of light

How to exploit them for optical applications → see Fauzia Jabeen presentation on Friday

Thank you !